

**Treatment of high organic, low toxicity wastewaters using a
soil biofilter system**

Project Completion Report

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Abstract

Large quantities of high organic content (usually expressed as BOD₅) wastewater are produced by industries and municipalities in Louisiana. Treatment of much of this wastewater is minimal and discharges have resulted in accelerated eutrophication and degradation of water quality in receiving water bodies. Land application systems such as overland flow treatment have the potential to inexpensively treat this wastewater. This study investigated overland flow treatment of wastewater from two Louisiana industries, alligator farm wastewater and sugar refinery wastewater, in laboratory-scale treatment systems. The chemical characteristics of the alligator farm wastewater resembles a strong domestic wastewater with double the normal N content.

Treatment of BOD in the soil biofilter system was demonstrated in these experiments (94% of the BOD in the sugar refinery canal wastewater and 64% of the alligator farm wastewater BOD was removed at a loading rate of 1 cm/day). In addition, the optimal detention time was determined for reducing the BOD in the alligator wastewater below secondary treatment standards. Removal of N from the alligator wastewater was very efficient with a 95% removal requiring a detention time of 150 minutes. Removal of P was less efficient due to the anionic form of this pollutant. The P capacity of the soil biofilter was estimated using P adsorption isotherms. Scale-up of the system for a working alligator farm was also performed based on current EPA design practices.

1. Treatment of high organic wastewater using soil biofilter beds.

Introduction

Discharges of untreated water and wastewater into water bodies in Louisiana contribute to reducing water quality across the state. These untreated waste streams originate from a variety of sources, municipal, rural and industrial. Water from these sources are discharged without treatment for several reasons: the lack of cost-effective treatment techniques for these types of waste streams, the isolated rural nature of some of these discharges and the ability to dilute these discharges in larger bodies of water. The contaminants in these wastewaters are diverse and include readily-degradable organic compounds, various forms of N and P, toxic organic compounds, metals, and microorganisms.

One type of wastewater of interest in Louisiana is water containing high concentrations of easily-degradable organic compounds (usually expressed as 5 day biochemical oxygen demand, BOD₅), N and P. These wastewaters are generally of low toxicity but can impact the aquatic environment by overloading natural aquatic systems with nutrients (N, P, and C). The result of these discharges is eutrophication and oxygen depletion in the water bodies receiving the wastewater. In many respects the composition of these wastewaters resembles municipal wastewaters but with higher concentrations of pollutants.

Many industries generate this type of wastewater in Louisiana. The present study has investigated water from two industries, sugar production and aquaculture. Sugar production, the milling and refining of sugar cane, produces large quantities of wastewater with high concentrations of readily-degradable carbon compounds (e.g., simple sugars). Current treatment of these wastewaters usually involves extended detention times (months) in oxidation ponds as the extremely high BOD of these wastes is satisfied. Other treatment methods include discharge of partially treated wastes into natural wetland systems which have a large capacity to assimilate carbon substrates.

The aquaculture industry is a growing industry that also produces large quantities of high-strength wastewater. Production and processing operations are scattered throughout the state. The farming of alligators is a sector of this industry that has seen recent growth with over 100 farms currently operating in the state. Alligator farming is generally conducted in buildings containing water-filled pens. Large quantities of wastewater (pen water and wash water) are generated daily with high BOD and nutrient

contents as the water is changed. Current treatment is generally accomplished by lagoon systems which result in a partially treated effluent. It is recognized that a better method of treatment is needed for the large quantities of wastewaters produced.

Land application concept

Most of the contaminants present in high strength, low toxicity wastewater are readily adsorbed by soil and thus may be adaptable to treatment using land application. Land application has the potential to treat wastewater because it removes contaminants from wastewater and places them in contact with the abundant and active soil microbial population where biodegradation and other transformations can occur (schematic, Figure 1). Soil functions as an adsorbent, such as activated carbon, that is continuously regenerating itself through natural microbial processes. The concept of soil treatment of waste is not new and is currently used on a large scale to treat municipal wastewater (Crites and Pound, 1976), industrial wastewater (Hunt et al., 1976) and waste gases (Bohn and Bohn, 1988). In addition, the potential of this concept has been demonstrated for other types of industrial wastes including PCB wastes (Pardue et al., 1988), mine wastewater (Kauffman et al., 1986) and oilfield wastes (Pardue et al., 1989).

The three types of land application systems in widest use are rapid infiltration, slow-rate infiltration, and overland flow. These systems differ in the way that the wastewater interacts with the soil and vegetation at the site. Since the proposed soil biofilter system closely resembles overland flow, the other types of land application treatment (rapid infiltration and slow-rate infiltration) will not be considered further.

Briefly, in overland flow treatment, wastewater is discharged across gently sloping vegetated terrain. Wastewater flows as a thin sheet across relatively impermeable soil and vegetation and is regenerated by a combination of biological, chemical and physical processes. Effluent is collected in a collection trench and is usually discharged directly without further treatment. Slope lengths of overland flow systems treating municipal wastewater range from 65 to 200 ft. with a grade of 2 to 8%. Vegetation is usually a mixture of grasses that serve to prevent erosion, act as a further support to soil microorganisms, and provides some storage for nutrients (EPA, 1981). The primary site of wastewater treatment, however, is on the soil particles, themselves, which support the biomass that degrades the pollutants.

An overland flow treatment system has the potential to treat high BOD wastewater from Louisiana industries. Treatment of the pollutants present in these wastewaters (N, P and C) has been demonstrated using municipal wastewaters. Also,

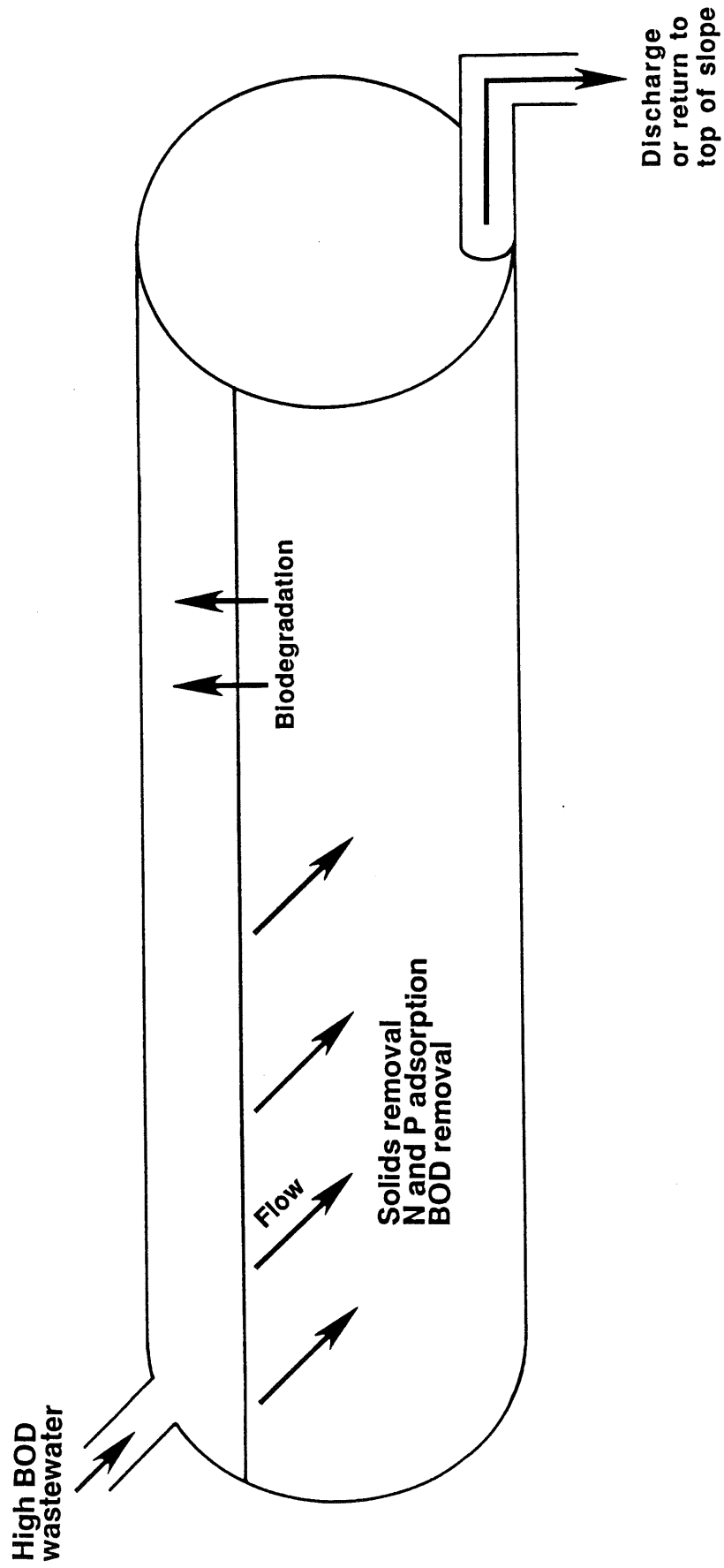


Figure 1. Schematic of proposed land application system for treating high BOD wastewater.

high BOD wastewaters from the food processing industry have been treated using overland flow systems. Brewery wastes with BOD₅ as high as 20,000 mg/L are routinely treated in Anheuser-Busch facilities across the U.S. (Keith and Lehman, 1986). Overland flow treatment systems are cost-effective, requiring low construction costs, low maintenance, and little or no energy requirements when compared to conventional treatment systems. Overland flow systems also require a slowly permeable soil such as the clayey soils of Louisiana. Also, overland flow systems are routinely added on as a polishing step to other treatment systems such as lagoons or oxidation ponds. Lagoons and oxidation ponds are commonly used to treat high BOD wastewaters in Louisiana.

Objectives

The objectives of this project were to demonstrate the application of a type of overland flow wastewater treatment to high organic, low toxicity waste streams generated in Louisiana. Experiments were conducted with wastewater from a sugar refinery discharge and pen wastewater from a large alligator farm. The specific objectives were to:

- (1). Establish the effectiveness of treatment of high-organic waste streams in laboratory model soil biofilter systems constructed from Louisiana soils. Experiments were conducted using models of a working treatment system with real-world high BOD wastewater.
- (2). Investigate the kinetics of BOD breakdown in the soil treatment system. Experiments were conducted on degradation of wastewater organic compounds in soil suspensions under controlled aeration conditions.
- (3). Investigate treatment efficiency of N and P fractions (tertiary treatment), both organic and inorganic during the treatment process. Optimal detention times for removal of ammonia, organic N and P were determined. The total capacity for the system to adsorb P was also determined. This information was used in a sample design of a working soil biofilter system.

Materials and methods

Land application models

Mississippi alluvial soil (Sharkey clay) was sampled from a field near Baton Rouge, LA. Soil was air-dried and ground to a uniform size to assure uniformity between treatments. A laboratory model of the soil biofilter system has been described by Pardue et al. (1988). The treatment system is a modified version of one developed by Chen and Patrick (1980). A schematic of the model is shown in Figure 2. The model was constructed from 0.5 cm thick plexiglass. The inside dimensions of the model were 100x10x10 cm (LxWxD). The inside edges of the model were sealed with silicon rubber to prevent leakage. A water collection trap was installed at the lower end to collect surface run-off. A drainage port at the lower end of the model collected sub-surface flow. All connecting tubing was Teflon FEP (Cole-Parmer).

Approximately 20 kg of the air-dried soil was uniformly packed in the model to a depth of 8 cm. Efforts were made to pack the replicates consistently. A small piece of glass wool was packed in the lower sections of the model to provide drainage in the subsurface outlet and to prevent excessive washout of soil from the system. The treatment system was prewetted with 3 consecutive application days of tap water. Wastewater was applied to the upper end of the model with a multichannel tubing pump (Cole-Parmer Masterflow pump 7567).

Wastewater application

Wastewater was applied to the system at a rate of one liter per day. This loading rate is equivalent to 1 cm/day. This loading rate is at the lower end of the recommended range of hydraulic loading rates specified in EPA's overland flow design manual (EPA, 1981). It was expected that a lower loading rate would be necessary to ensure adequate treatment of the high BOD present in the waste. Wastewater was applied on a 5 day per week schedule with a two day resting period. Volumes of surface and subsurface flows were measured daily and subsamples were removed for BOD₅, N, and P analyses.

Wastewater was applied for a four week period for both the sugar refinery and alligator farm samples. Further experimentation was performed using the alligator farm wastewater. Following the four week application period, an experiment was conducted to establish the effective loading rate for any given discharge criteria. Wastewater was applied according to the same schedule as described above. However, for five

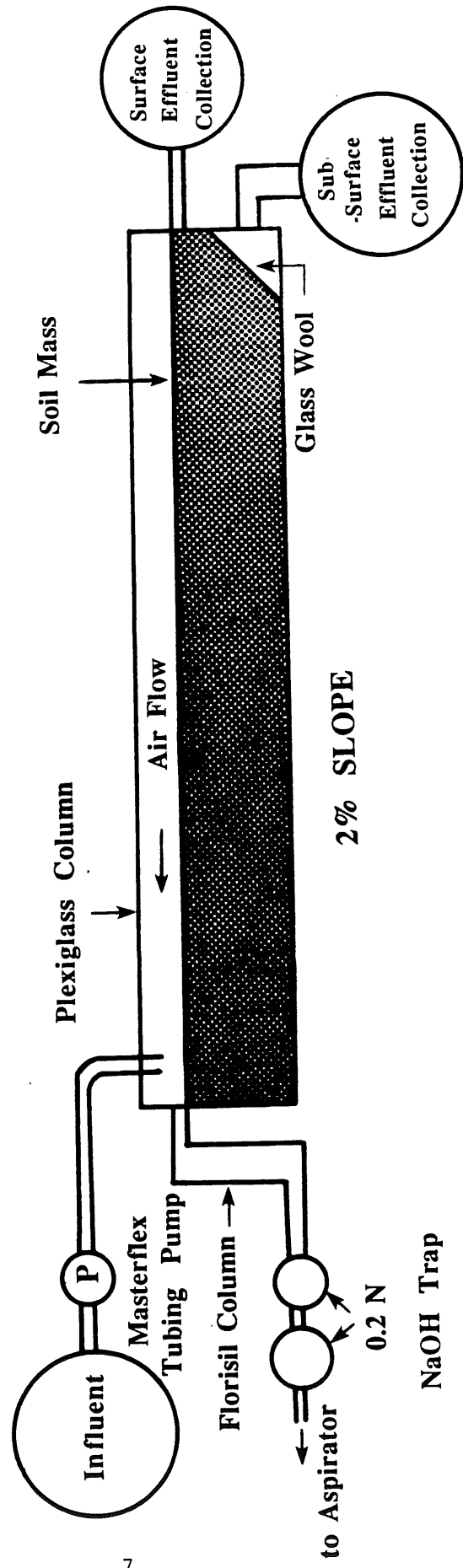


Figure 2. Laboratory model of land application system.

consecutive days the wastewater recovered from the end of the system was used as the influent wastewater for the following day. This allowed an optimal loading rate to be calculated from the decrease in BOD, N and P. Following this experiment, a separate experiment with a slower application rate (0.5 cm/day) was used to determine detention times necessary to achieve very low BOD concentrations.

Detention time

Detention time was determined using the method of Martel et al. (1982). Briefly, a spike of Cl^- , as NaCl , was added to the top of the system when saturated. Fractions of the effluent were removed every 5-15 minutes and analyzed for chloride using titration with AgNO_3 (Standard Methods, 1976). Average detention time was taken as the time of maximum Cl^- concentration.

Pollutant Analyses

Five day biochemical oxygen demand (BOD_5) was measured using standard methods. Dilutions of raw and discharged wastewater were incubated at 25°C for 5 days. No wastewater seed was necessary during incubation. Dissolved oxygen was measured using an oxygen electrode (Lazar Research Laboratories).

Inorganic nitrogen (ammonia) was determined by distillation into boric acid indicator solution. Nitrate/nitrite was determined on the same aliquot by distillation after addition of Devarda's alloy. Total kjeldahl nitrogen was determined by distillation into boric acid after block digestion (sulfuric acid:potassium sulfate:mercuric sulfate solution, 200°C for 4 hours, 370°C for 1 hour) (Plumb et al., 1981). Sodium hydroxide (15 N) was added to the digested sample within the distillation apparatus to convert ammonium ion to ammonia. Organic nitrogen was calculated as the difference between TKN and inorganic nitrogen (ammonia).

Attempts were made to fractionate P into organic and inorganic fractions. However, the presence of bleach (sodium hypochlorite) in the sample interfered with colorimetric determination of orthophosphate (PO_4^-). Therefore, subsamples were filtered through $0.45\ \mu\text{m}$ filters and an aliquot analyzed using ICP. This analytical technique cannot distinguish between inorganic and organic P, however.

Other techniques used to characterize the alligator farm wastewater included measurement of pH and conductivity using appropriate meters. Measurement of major cations (Ca, Mg, and Na) using ICP was also conducted in order to calculate the sodium

adsorption ratio (SAR) which gives an indication of the irrigation quality of the wastewater.

Data analysis

Data was compiled and analyzed using SAS (Statistical Analysis System, Cary, N.C.). Repeated loading data were fitted to first-order decay equation using non-linear regression (Marquardt algorithm, PROC NLIN).

Results and Discussion

Wastewater characteristics

Chemical characteristics of the alligator farm wastewater are presented in Table 1. The BOD₅ of the sugar refinery canal wastewater was 110 mg/L and since this would not be considered a very high BOD wastewater no further chemical analyses were conducted. Specific comparisons between the alligator farm wastewater and other types of wastewater are presented in the text of the report. However, in summary, the chemical characteristics of alligator farm wastewater resembles a very strong domestic wastewater with a high N content.

BOD Removal

Removal of BOD from the sugar refinery canal wastewater is presented in Figure 3. Initial BOD of the sugar wastewater was 110 mg/L. Average BOD in the effluent was 4 mg/L (removal efficiency=94%). Nearly all of the BOD was satisfied within the system at this loading rate (1 cm/day). Average effluent BOD was near the maximum possible removal reported for BOD in land application systems.

Comparisons between common BOD values for domestic wastewater and the samples used in this study are presented in Table 2. The sugar refinery canal wastewater is comparable to a weak domestic wastewater and probably would not be considered a "high" BOD sample. Nevertheless, the removal of BOD has been demonstrated in this system and it has the potential to treat samples with higher concentrations of organics.

The alligator farm wastewater has a BOD concentration comparable to a strong domestic wastewater. Removal of BOD from the alligator wastewater is presented in Figure 4. Wastewater was applied at the same hydraulic loading rate as the sugar

Table 1. Alligator farm wastewater characteristics

BOD ₅ , mg/L	452
pH	6.9
Conductivity, μ mhos	650
TS, mg/L	379
VSS, mg/L	219
Total P, mg/L	10.9
Soluble P, mg/L	7.6
NH ₃ , mg/L	77.5
NO ₃ ⁻ , mg/L	4.6
TKN, mg/l	153.4
Ca, mg/L	13.4
Mg, mg/L	5.0
Na, mg/L	14.8
Sodium adsorption ratio [Na]/([Ca+Mg]/2) ^{0.5}	0.73

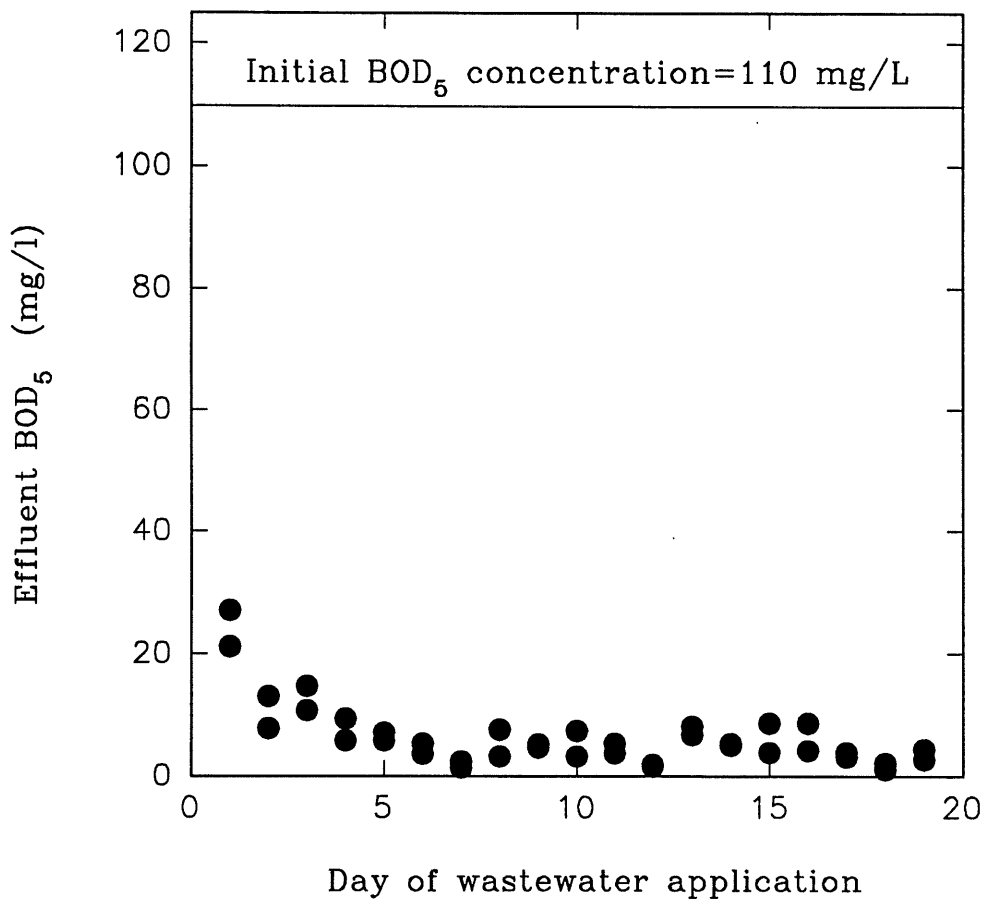


Figure 3. Removal of BOD from sugar refinery wastewater in land application system at 1.0 cm/day loading rate.

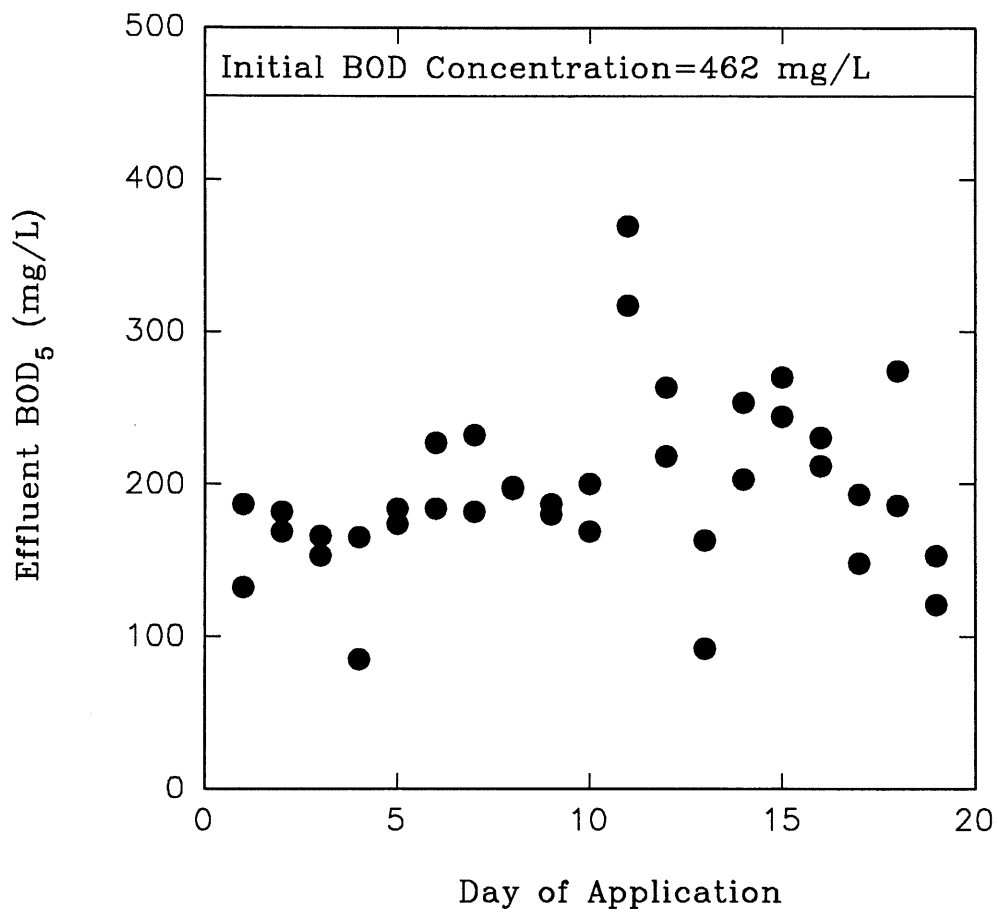


Figure 4. Removal of BOD from alligator farm wastewater in land application system at 1.0 cm/day loading rate.

refinery canal wastewater (1 cm/day). This application rate resulted in a detention time of wastewater in the system of 35 minutes (Figure 5). Average BOD in the effluent was 196 mg/L (removal efficiency=59%) at this detention time. Comparison of concentrations of BOD in the influent and effluent of overland flow systems does not give a true indication of the total removal of BOD since evaporation removes a significant portion of the water volume. When the BOD removed is expressed on a mass basis, efficiency was 64%.

Table 2. BOD₅ content of wastewater. Domestic wastewater data are from Metcalf and Eddy (1979).

Sample	BOD (mg/L)
Domestic Wastewater	
Strong	400
Medium	220
Weak	110
Alligator farm wastewater	452
Sugar refinery canal wastewater	110

At this detention time BOD was reduced only to a level of 196 mg/L. Since conventional secondary treatment can reduce BOD to 15-25 mg/L it is obvious that the alligator wastewater will require a longer detention time to reach this standard. Therefore, the optimal detention time for two loading rates was determined by repeated loading onto the laboratory system. The results from these experiments is presented in Figure 6. Experiments were conducted at application rates of 0.5 cm/day and 1.0 cm/day with total detention times ranging from 35 min. to 525 min. Data were fit to a first-order decay equation given as:

$$C_s = C_0 e^{-kt}$$

where C_s is the pollutant concentration at any distance along the slope,

C_0 is the initial pollutant concentration,

k is the first-order rate coefficient (time^{-1}) and

t is time.

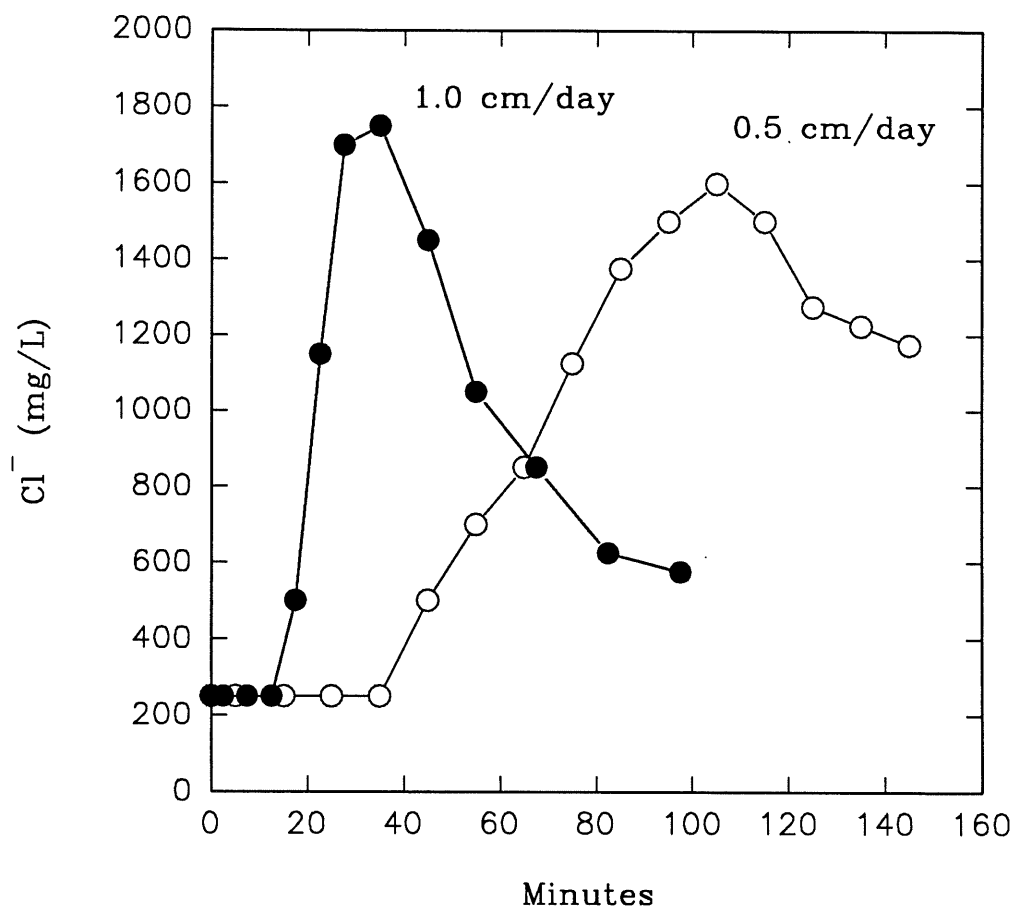


Figure 5. Detention time measurement using Cl^- as a conservative tracer for loading rates of 0.5 and 1.0 cm/day.

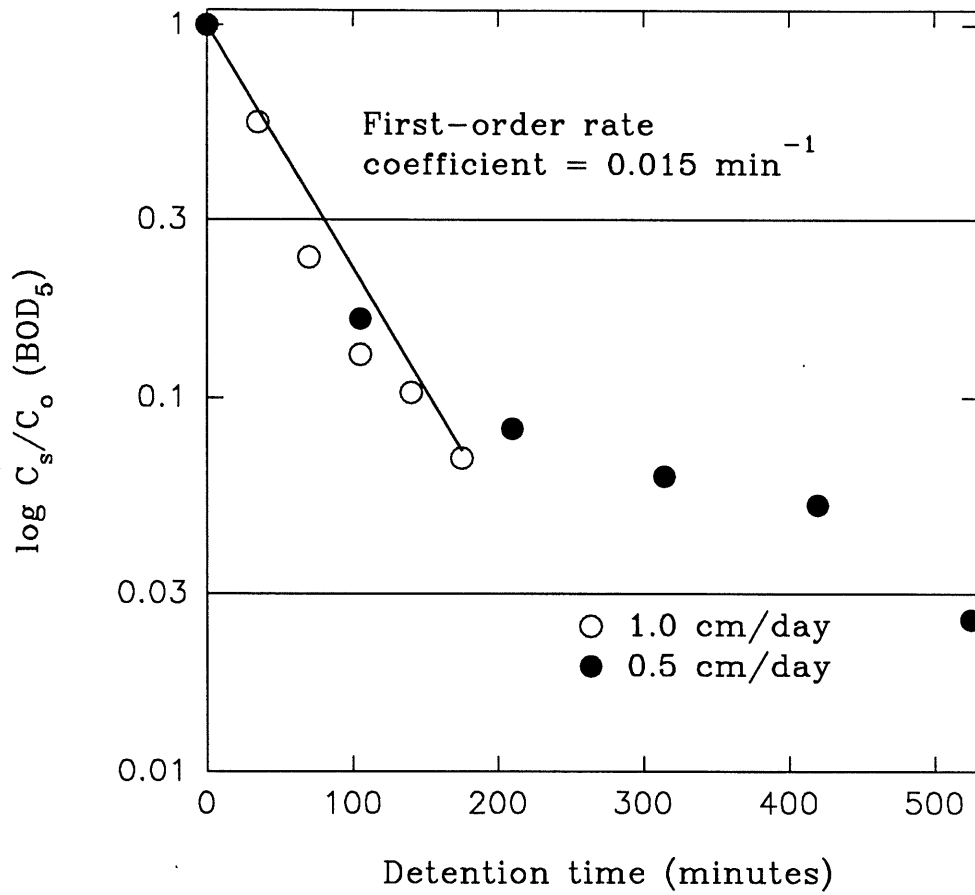


Figure 6. Removal of BOD during repeated application of alligator farm wastewater. Data are plotted as a first-order removal process. Experiments performed at two loading rates (0.5 cm/day and 1.0 cm/day).

Data are plotted in the linearized form:

$$\ln(C_s/C_0) = -k*t$$

BOD was removed with a first-order rate constant of 0.015 min^{-1} at a loading rate of 1 cm/day. At a lower loading rate (0.5 cm/day) the removal of BOD fit the first-order equation initially until the detention time increased where the curve levels off. It is unclear why very long detention times were needed to reduce BOD levels below 20 mg/L. Leaching of oxygen-demanding substances from the soil into the effluent and the difficulty in measuring low levels of BOD may have contributed to this result. For the purposes of this study the rate constant derived from the higher loading rate will be used for system design. It is clear that longer detention times are necessary to remove high concentrations of BOD from alligator farm wastewater than from domestic wastewater. Removal of 80% of the BOD from the alligator wastewater would require a detention time of 107 minutes, while 80% removal of BOD in primary wastewater required approximately 40 minutes (Martel et al., 1982; data from CRREL and Davis, California overland flow systems).

Overall, the treatment system was able to treat the high concentrations of BOD present in these wastewaters. Removal of BOD below secondary treatment standards will require longer detention times than commonly used for overland flow treatment of domestic wastewater.

N removal

Overland flow systems are also considered highly effective at advanced wastewater treatment (removal of N and P). Conditions in overland flow systems are conducive to nitrification/denitrification reactions that can result in removal of both ammonium and nitrate. Removal of N and P in overland flow systems have been previously studied in our laboratory (Chen and Patrick, 1980; Khalid and Patrick, 1980).

Removal of N is particularly important in this wastewater because of high N content. The N content of the alligator wastewater is compared to common values of N in domestic wastewaters in Table 3. The alligator farm wastewater has total N and organic N values twice the levels of even the strongest domestic wastewater. Ammonia levels are 1.5 times higher and nitrate levels are detectable in the alligator farm wastewater.

Table 3. N content of wastewater. Nitrogen levels in domestic wastewater are from Metcalf and Eddy (1979).

Sample	Total N	Organic N	NH ₃	NO ₃ ⁻
Domestic Wastewater				
Strong	85	35	50	0
Medium	40	15	25	0
Weak	20	8	12	0
Alligator farm wastewater	154	76	78	4.60

Elevated levels of nitrogen are likely due to the physiology of the alligator, itself. An alligator may excrete 150 mEq of ammonium salts per day (for a 70 kg animal) while man (70 kg) excretes 30-35 mEq per day (Coulson and Hernandez, 1983). Ammonia constitutes 50% or more of the excreted N in alligators as compared to 5-10% of the excreted N in man (Coulson and Hernandez, 1983). This elevated level of nitrogen in alligator wastewater is another reason to consider the use of land application with its ability to effectively remove and process large quantities of N.

The removal of organic N is demonstrated in Figure 7. Average values of organic N after one cycle through the system (detention time = 35 minutes) were 22.6 mg/L (70 % removal). On a mass basis the average removal averaged 75 %. Organic N was removed very efficiently in the system. Further reduction in organic N would be desirable even though total N values in conventional secondary treatment fall between 20-60 mg/L. Therefore, measurement of organic N was also made during the repeated loading experiments. The kinetics of removal of organic N is presented in Figure 8. Organic N was removed with a first-order rate constant of 0.029 min⁻¹. The organic N concentration of the effluent decreased rapidly to less than 2% of the organic N added after a detention time of 130 minutes.

The removal of ammonia is presented in Figure 9. Ammonia, present in the ammonium ion form at this pH, averaged 40.1 mg/L (46 % removal) after one cycle through the system. On a mass basis the average removal averaged 50%. Further removal of ammonia-N is also desirable so ammonia was analyzed during the repeated loading experiment. The kinetics of removal of ammonia is presented in Figure 10. Ammonia-N was removed with a first-order rate coefficient of 0.023 min⁻¹. Removal of ammonia-N to levels less than 5% of the original concentration require a detention time of only 130 minutes.

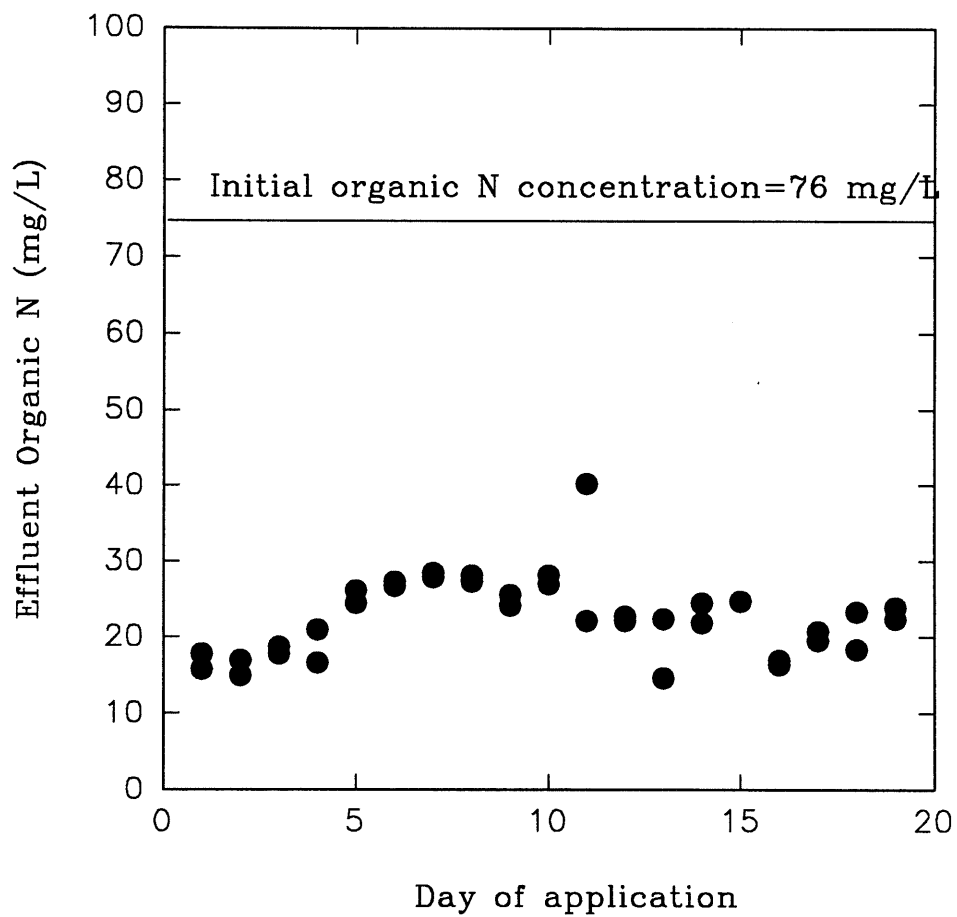


Figure 7. Removal of organic N from alligator farm wastewater in land application system at 1.0 cm/day loading rate.

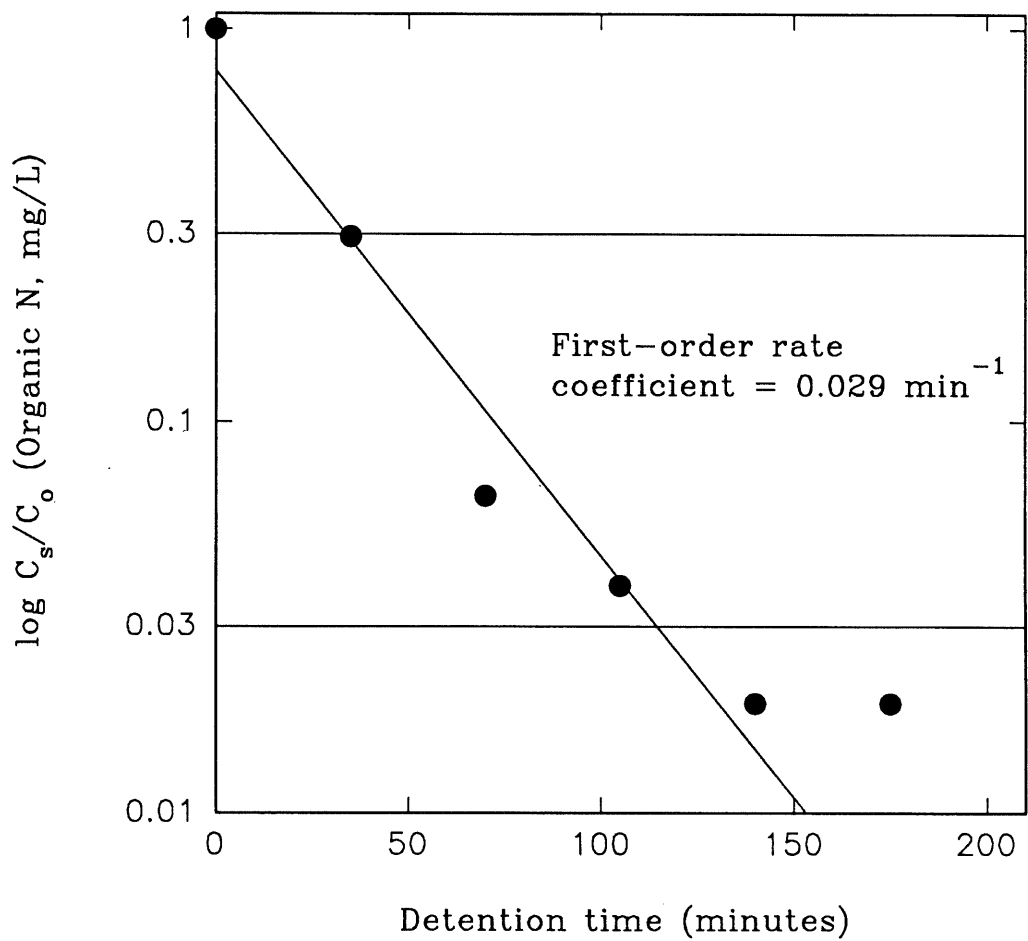


Figure 8. Removal of organic N during repeated application of alligator farm wastewater. Data are plotted as a first-order removal process. Experiment performed at 1.0 cm/day loading rate.

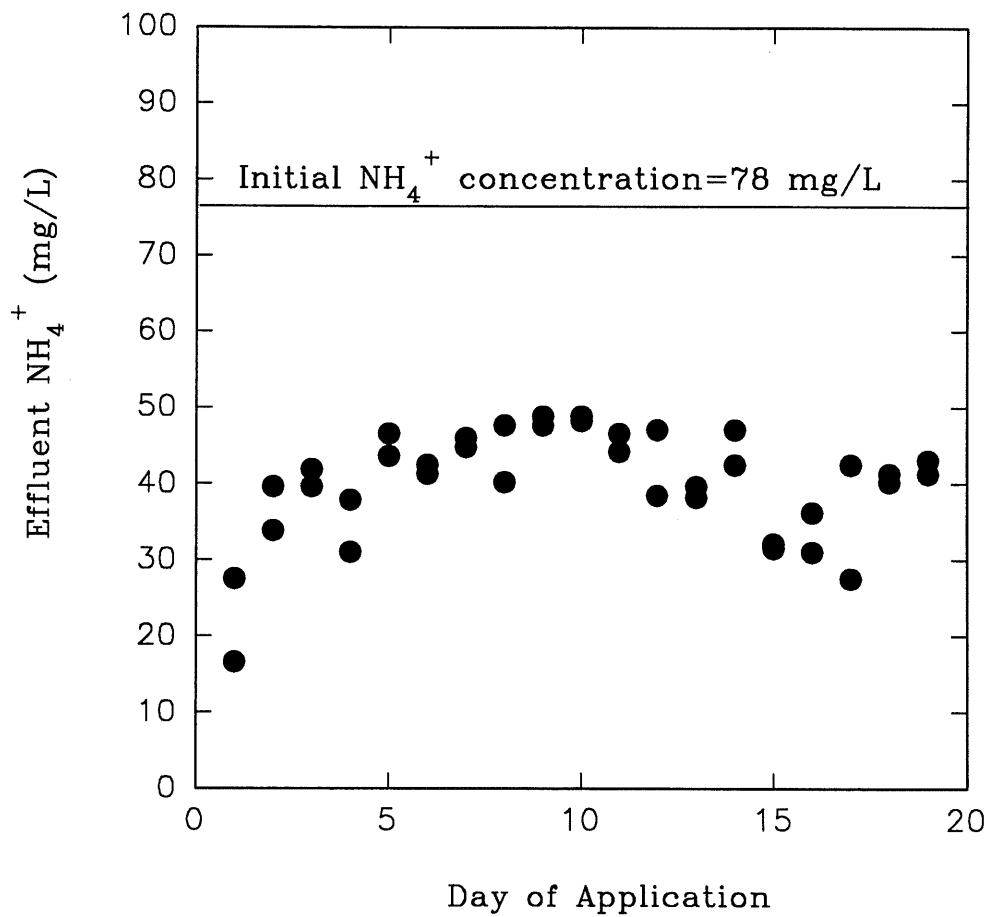


Figure 9. Removal of ammonia N from alligator farm wastewater in land application system at 1.0 cm/day loading rate.

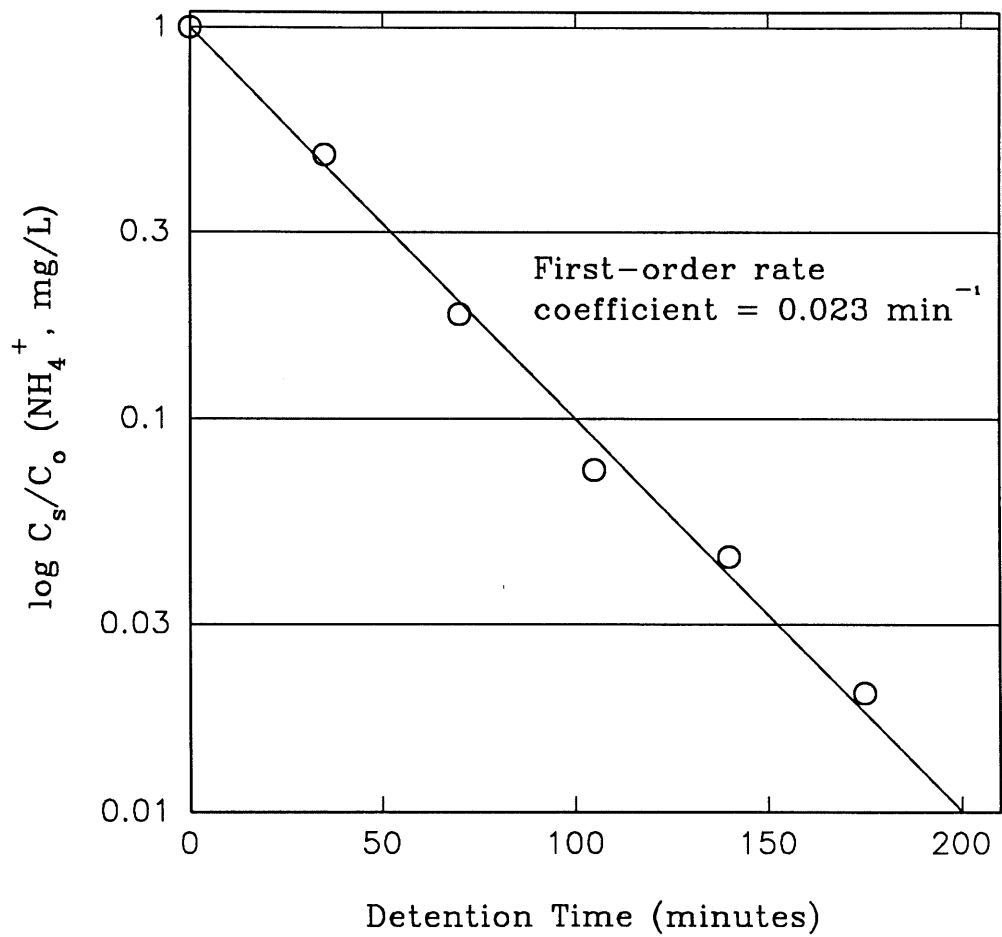


Figure 10. Removal of ammonia N during repeated application of alligator farm wastewater. Data are plotted as a first-order removal process. Experiment performed at 1.0 cm/day loading rate.

Overall, the soil biofilter system was efficient at removing N. Mechanisms probably included adsorption of NH_4^+ and organic N forms, nitrification-denitrification reactions and mineralization of organic N forms. Nitrate was barely detectable in the samples of effluent (data not shown, $< 2.0 \text{ mg/L}$).

P removal

The removal of P in overland flow systems is much less efficient than say, ammonium, since P is present primarily in an anionic form, (as PO_4^-). Removal of P can occur, however, through adsorption and precipitation reactions although the capacity for the assimilation of P in soils is finite. Therefore, when removal of P is a requirement, the capacity of the soil for P can determine the length of time a land application system can operate. Removal of P is discussed in more detail later in this report.

Typical values of P for domestic wastewater are compared with the P content of the alligator farm wastewater in Table 4. As stated earlier it was difficult to fractionate P into organic and inorganic fractions due to interference from bleach added to the wastewater. However, measured levels of soluble and total P (incorporating both inorganic + organic fractions) indicate that P levels are equivalent to a medium domestic wastewater.

Levels of soluble P in the effluent are presented in Figure 11. Average values of soluble P in the effluent was 5.7 mg/L . P was not removed very efficiently (25 %) in the system at this detention time and loading rate. Moreover, removal efficiency decreased as more wastewater was added to the system (Figure 11). This decrease in removal efficiency (a trend which also occurred within each application week) was likely due to the high BOD loading rate which created anaerobic conditions within the system. As discussed in the next section, anaerobic soils have a much lower capacity to adsorb P than aerobic soils.

The kinetics of P removal in the repeated loading experiment is shown in Figure 12. As expected, removal of P had the lowest first-order rate coefficient of the pollutants measured (0.008 min^{-1}). A detention time of 85 minutes would be required to reduce P concentrations below 50% of the influent. Fortunately, P concentrations in the alligator wastewater are not excessively high. In fact, secondary treatment of domestic wastewater can only reduce P levels to $6\text{-}15 \text{ mg/L}$. In wastewaters with higher P content initial treatment with alum, possibly in the lagoon or holding pond itself, may be necessary to reduce P to discharge limits.

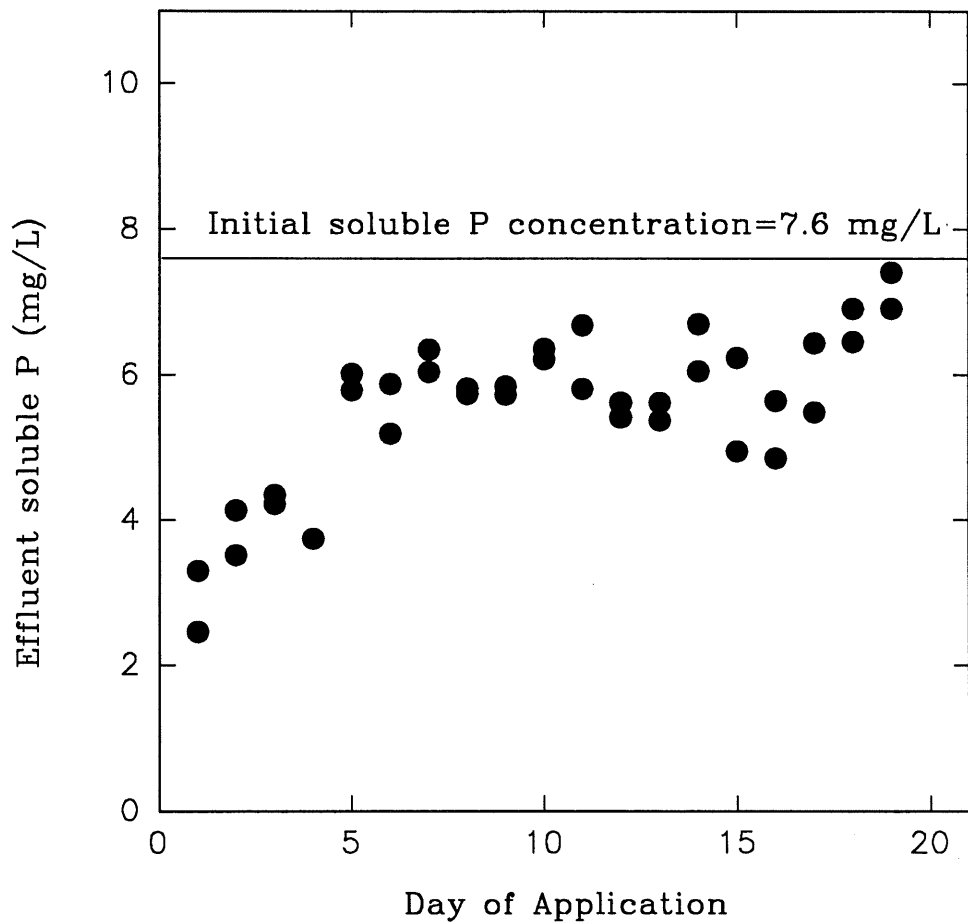


Figure 11. Removal of soluble P from alligator farm wastewater in land application system at 1.0 cm/day loading rate.

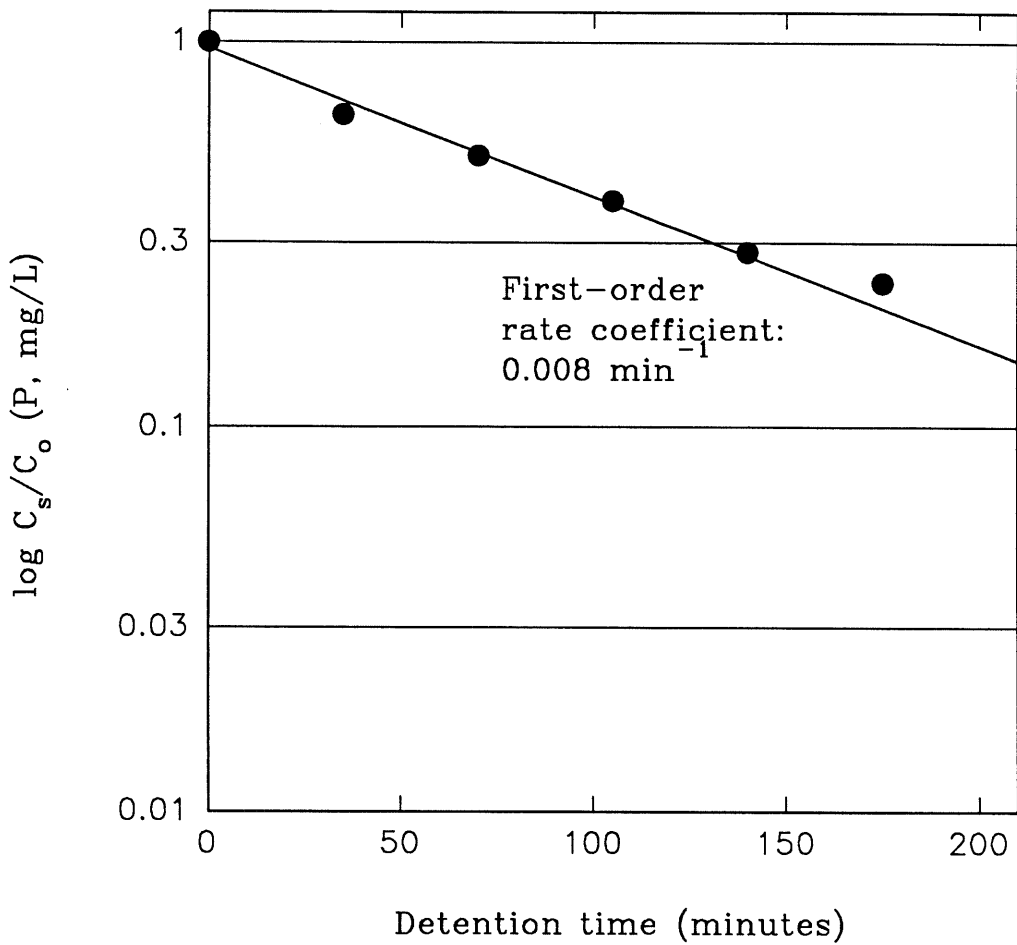


Figure 12. Removal of soluble P during repeated application of alligator farm wastewater. Data are plotted as a first-order removal process. Experiment performed at 1.0 cm/day loading rate.

Table 4. Phosphorus concentrations in alligator wastewater and typical domestic wastewater (domestic wastewater values from Metcalf and Eddy, 1979).

Wastewater	Inorganic P (mg/L)	Organic P (mg/L)	Total P (mg/L)
Alligator farm	-	-	soluble (7.6) total (10.9)
Domestic			
Strong	10	5	15
Medium	5	3	8
Weak	3	1	4

In summary, the soil biofilter beds removed BOD, ammonia-N, organic-N, and P from the alligator farm wastewater. Detention times necessary to affect removal of BOD, N and P were determined and can be used in system design. Differences in the rate of removal of different pollutants were noted from the kinetic experiments. For example, removal of P will require a longer detention time (and hence, a larger biofilter system) than the removal of an equivalent percentage of ammonia-N.

2. Phosphorus Capacity of Soil Biofilter Beds

Introduction

Release of phosphorus present in wastewater can accelerate eutrophication in water bodies such as lakes and streams (e.g., Vollenweider, 1976). Removal of P, therefore, is a goal of wastewater treatment. Municipal wastewater treatment facilities, however, contribute a large fraction of the P entering natural water bodies (Hasler, 1968). Land application systems such as overland flow treatment systems are more efficient at removing phosphorus when properly managed. Reported removal efficiencies of P in overland flow systems vary widely (10-89%) and depended on the type of wastewater and the season of application (Khalid et al., 1980). Several studies have been conducted investigating the retention of phosphorus in overland flow systems (e.g., Khalid et al., 1981; Holford and Patrick, 1979).

Phosphorus removal during overland flow is accomplished primarily by sorption and precipitation reactions with iron, aluminum, and calcium compounds in soil. Plant uptake also plays a minor role in phosphorus immobilization in overland flow systems. Soils have a limited capacity for phosphorus uptake. When available adsorption sites for P are filled, the overland flow system virtually ceases to adsorb P and may begin to release more P than is loaded onto the soil. Therefore, the phosphorus capacity of the soil in the land application site is of primary importance in determining the level of P treatment and ultimately, the length of time wastes can be applied at the site.

Adsorption isotherms can be used to estimate the length of time a land application facility can continue to adsorb P. Knowing the P content of the wastewater, the capacity of the soil to retain P, and the depth of the contact zone, a simple calculation can be made to determine the length of time P removal would occur. P isotherms were constructed on the Sharkey clay used in these overland flow systems and the results are presented below.

Methods and materials

P isotherms

A subsample of the Sharkey clay soil used in the treatment systems was homogenized and made up with deionized water to a 5:1 (water:soil) suspension. The soils were incubated in stirred suspension microcosms (Patrick et al., 1973) under aerobic (air-purged) or anaerobic (Ar-purged) conditions (Figure 1). Samples were allowed to equilibrate for 14 days before sampling. Subsamples of the suspensions (20 mL) were

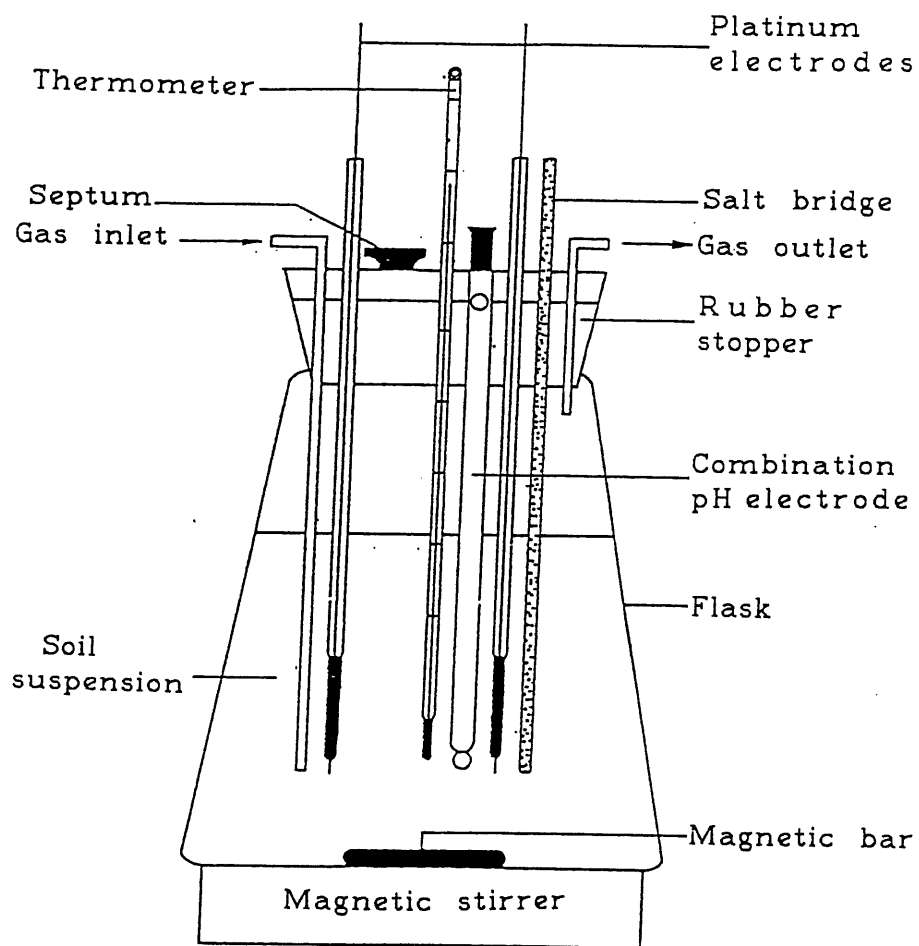


Figure 1. Controlled redox-pH microcosm.

removed with a syringe and placed in centrifuge tubes filled with air (aerobic treatment) or argon (anaerobic treatment). An aliquot of a P standard (as Na₂PO₄) had been previously placed in the gas-purged centrifuge tube. Samples were shaken on an oscillating shaker for 24 hours to allow contact between the P and the soil. Samples were centrifuged (5000 rpm, 15 minutes, Sorvall refrigerated centrifuge, SA-600 rotor) and filtered through 0.45μ filters under the appropriate atmosphere. Samples were analyzed for P using ICP.

Data were fit to Freundlich and Langmuir isotherms using non-linear regression (Marquardt algorithm, PC-SAS, Cary, N.C.). Equations were in the following forms:

Langmuir:
$$x/m = K \cdot C \cdot b / (1 + K \cdot C)$$

Freundlich:
$$x/m = K' \cdot C^{1/n}$$

where C is the equilibrium concentration of P in solution,

x/m is the weight of adsorbed P per unit weight of soil,

K (Langmuir) is a constant related to binding strength,

b (Langmuir) is the maximum amount of P that can be adsorbed,

K' (Freundlich) is an empirical constant,

n (Freundlich) is a second empirical constant.

Results and Discussion

P isotherms

Phosphorus isotherms for the aerobic and anaerobic soil suspensions are presented in Figure 2. The data show that for a given level of adsorbed P, soluble P in the anaerobic soil was several times higher than soluble P in the aerobic soil. This increase in soluble P as soil becomes anaerobic has been widely reported and is due to reduction of ferric iron compounds under anaerobic (low redox potential conditions) (e.g., Patrick and Khalid, 1974). Ferrous (Fe⁺²) compounds are much more soluble than ferric (Fe⁺³) compounds. For this reason anaerobic soil has a lower capacity to adsorb P than aerobic soils.

The differences between P adsorption under aerobic and anaerobic conditions has important implications for P retention in land application treatment such as that proposed here. Excessive loading of high BOD wastewater onto the system can create anaerobic conditions throughout the contact zone. Evidence of this process was seen in the

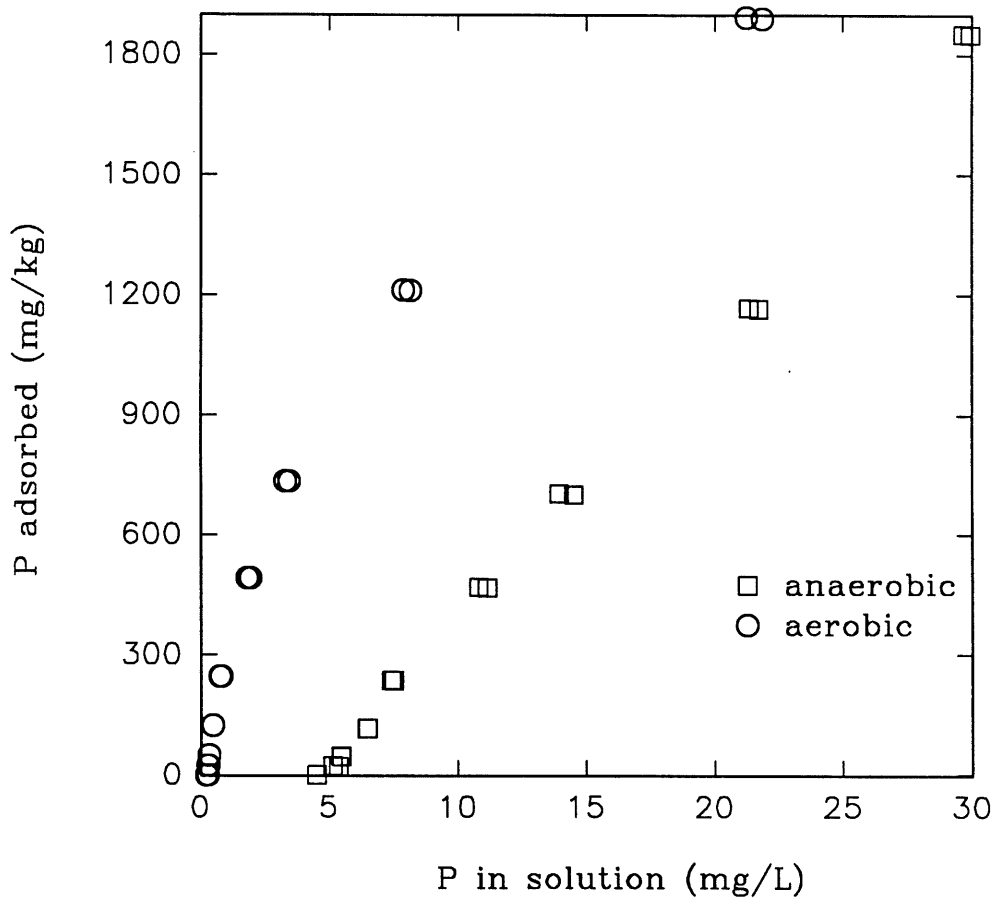


Figure 2. Adsorption isotherm for P under aerobic and anaerobic soil conditions.

experiments previously described where P breakthrough increased within each week of application. Development of completely anaerobic conditions could result in the release of large quantities of P already adsorbed to or precipitated as ferric compounds. Anaerobic conditions will also retard adsorption of newly added P.

Quantitatively, fitting sorption isotherm equations to data such as in Figure 1 allows comparison between different soil and conditions. Table 1 presents the fitted parameters from the Freundlich and Langmuir isotherms. These are the two most common isotherms used in sorption studies. The parameters of the Freundlich isotherm, K' and n , are purely empirical and are primarily used for comparative purposes. The parameters of the Langmuir isotherm, on the other hand, have a theoretical basis, K is an indicator of binding strength and b is a measure of adsorptive capacity. The shape of the anaerobic isotherm prevented the Langmuir equation from converging during the regression procedure. Unlike the aerobic sample the isotherm curve does not "turn over" as the P capacity is approached. This is likely due to precipitation processes removing P from solution at higher P concentrations under anaerobic concentrations.

Table 1. Langmuir and Freundlich isotherm parameters.

Treatment	Freundlich			Langmuir		
	K'	n	RSS	K	b	RSS
Aerobic	269.9	1.36	67,664	0.13	2373	26,666
Anaerobic	7.1	0.60	88,840	-	-	-

These data quantitatively indicate the increased P capacity of aerobic soils (Langmuir $q=2,373$ mg/kg). The inefficiency of P adsorption under anaerobic conditions can be seen by the increased concentration of soluble P for a given amount of adsorbed P. As stated earlier, P capacity can be used to estimate the length of time a land application system can remain in operation until the P capacity is exceeded. This calculation is presented in Table 2. The example used here is for an alligator farm of 2000 animals (2 gallons per animal per day) resulting in 4000 gpd (15.1 m³/day) of wastewater. The calculation results in an expected lifetime of 7.3 years if aerobic conditions are maintained in the contact zone. If anaerobic conditions are allowed to develop the expected lifetime of the site would be less.

Previous investigations of P removal on overland flow slopes have indicated that soil amendments such as lime may increase the removal of P during overland flow (Khalid et al., 1982). When concentrations of P are important, alternate methods of P removal (e.g., alum addition to the holding pond) may be necessary. Fortunately, concentrations of P in alligator wastewater are not excessively high. However, discharge of large amounts of this wastewater to a receiving water body could adversely impact the system over the long term. This study has determined that overland flow systems have only a limited capacity for P. Siting and design of working systems should consider the finite nature of these treatment systems with respect to P.

Table 2. Calculation of P (as PO_4^-) adsorption capacity in land application systems.

- Assumptions: 1). P in wastewater reaches equilibrium with soil in land application system.
 2). Wastewater P compounds react as PO_4^- .
 3). P adsorption can be modelled using Langmuir isotherm.

System parameters: Wastewater flow, Q (4000 gpd): $15.1 \text{ m}^3/\text{day}$
 Application rate, q: $0.05 \text{ (m}^3/\text{day}\cdot\text{m of width)}$
 Application schedule: 5 d/week (52 wk/year)
 Slope length, L (m): 40
 Slope width (m): 25
 Soil:wastewater contact depth, D (cm): 0-3
 Soil bulk density (g/cm^3): 1300 kg/m^3

Wastewater characteristics: P concentration: 8 mg/L
 P adsorption capacity: 2,373 mg/kg

1). Calculate soil mass:

$$(\text{Slope length}) \cdot (\text{Slope width}) \cdot (\text{contact depth}) \cdot (\text{soil bulk density}) = (\text{soil mass})$$

$$50 \text{ m} \cdot 50 \text{ m} \cdot 0.03 \text{ m} \cdot 1300 \text{ kg/m}^3 = 97,500 \text{ kg}$$

(2). Calculate soil P capacity = (soil mass) * (unit mass soil P capacity) = (soil P capacity)

$$97,500 \text{ kg} \cdot 2,373 \text{ mg/kg} = 231 \text{ kg P}$$

(3). Calculate wastewater P allowed = (soil P capacity) / (wastewater P concentration) =

$$231 \text{ kg P} / 8 \cdot 10^{-3} \text{ kg/m}^3 = 28,921 \text{ m}^3$$

(4). System lifetime = (wastewater P allowed) / (application rate) =

$$28,921 \text{ m}^3 / 3926 \text{ m}^3/\text{yr} = 7.37 \text{ yr.}$$

3. Kinetics of Alligator Waste BOD Degradation

Introduction

Experiments using the overland flow models allow calculation of removal efficiency and optimal loading rates, however, no information is gained on how fast organic compounds are degraded on a soil weight basis. This information may be particularly useful in the design of a working land application system. Further investigation into the degradation of the organic compounds present in the alligator farm wastewater was undertaken using controlled microcosms. These microcosms allow precise control of aeration conditions in the soil. The importance of maintaining aerated conditions in the surface contact zone has been emphasized. This experiment will also demonstrate the difference in the speed of breakdown of organic contaminants under aerated and anaerobic conditions.

The organic compounds applied to the soil can be removed by several mechanisms. The compounds can be sorbed or filtered out when the solids are removed. Organic compounds can subsequently be degraded by microorganisms, the most common carbon end products being CO₂ or microbial cell components. Both of these mechanisms are important in removing organic compounds within the biofilter system. This experiment will investigate the time frame of decrease in BOD in the soil solution after addition of wastewater.

Materials and Methods

Soil:water microcosms

Soil:water microcosms were constructed with the Sharkey clay soil (5:1 water:soil ratio). Microcosms were incubated as described in Patrick et al. (1973). Aerobic (air-purged) and anaerobic (Ar purged) microcosms were used as treatments. Microcosms were incubated for 2 weeks before addition of alligator wastewater. Background levels of CO₂ were also measured for several days before addition of wastewater.

Raw wastewater was added at the following rates over a 4-day period, 50 mL, 100 mL, 150 mL and 200 mL. After each wastewater addition the effluent gas stream from the microcosm was connected to two traps containing 30 mL of 1 N NaOH solution. Traps were changed over a 24 hour period measuring CO₂ emission during the

following time periods: (0-4 hr, 4-8 hr., 8-12 hr., 12-24 hr.). CO₂ was quantified by titration with a standard acid according to the method described in Anderson (1982).

During the final day of wastewater addition subsamples of the suspensions were removed to analyze for BOD. Subsamples (20 mL) were removed with a syringe and centrifuged (5000 rpm, 15 minutes) and filtered (0.45 μm) under an air or Ar atmosphere. Samples were removed according to the following schedule (0,2,4,6,8,14, and 24 hours). BOD was determined as described earlier.

Data analysis

Non-linear regression of the BOD data was performed using PROC NLIN in SAS (Cary, N.C.). Data were fit to both first-order decay and double-exponential decay equations.

Results and Discussion

BOD decay in the microcosm is presented in Figure 1. BOD was removed in the aerated suspension but not in the anaerobic suspension. It is obvious that "oxygen demand" will not be satisfied in the anaerobic suspension. However, much of the oxygen demand is organic compounds degradable under aerobic conditions. The anaerobic treatment was analyzed to demonstrate the problems that can be encountered when the loading rate creates oxygen-limited conditions in the contact zone.

Decay of BOD in the aerobic suspension occurred primarily over the first 4 hours after wastewater addition. BOD levels stabilized at around 60 mg/L. This would possibly indicate some limitation in reducing BOD even further, possibly a P or N deficiency. Other sources of BOD, e.g. decomposition of naturally occurring organic matter, may also keep levels of BOD high in the soil solution.

The decrease in BOD was not modelled well by a first-order rate equation. The initial decrease in BOD is very rapid and therefore, a double exponential decay equation was used to fit the data. The double exponential decay equation is given as:

$$C = ae^{-k_1 t} + be^{-k_2 t}$$

where C is the concentration of BOD at any time t and a,b,k1 and k2 are constants.

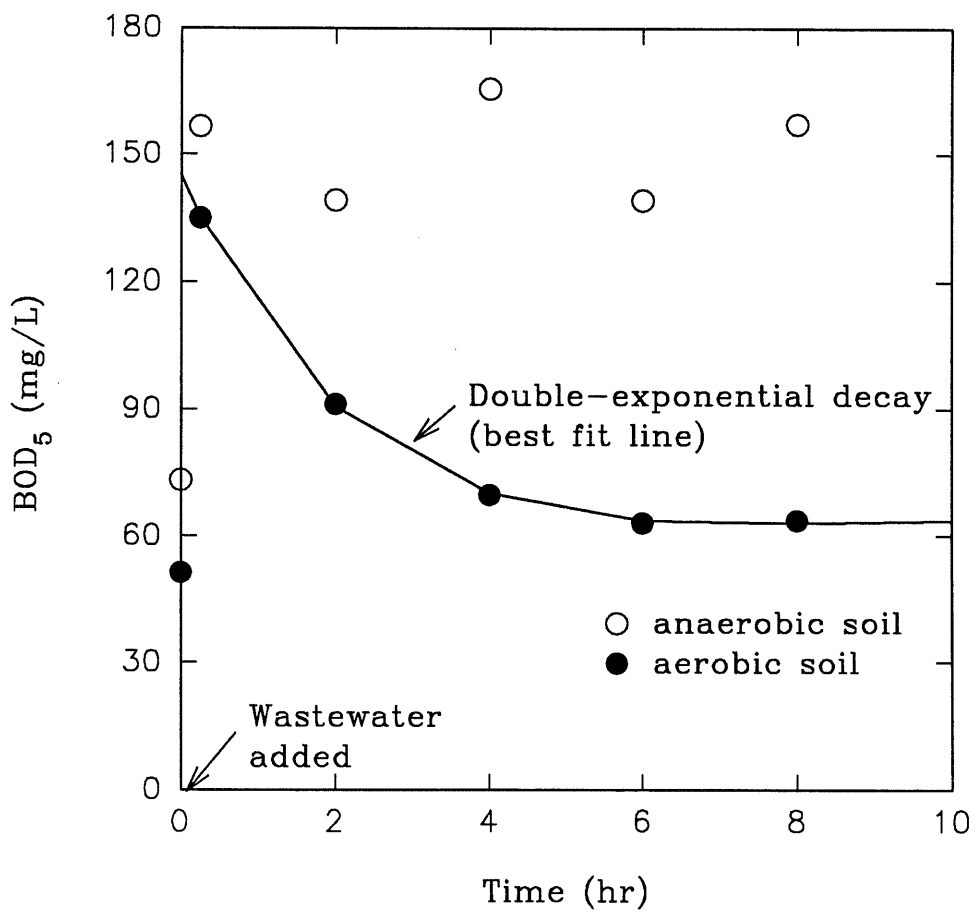


Figure 1. Decay of BOD in controlled microcosms under aerobic and anaerobic conditions. Solid line is from non-linear fit of double-exponential decay equation.

As demonstrated in Figure 1 this equation fit the data very precisely with a small residual sum of squares.

The release of CO₂ from the microcosms is seen in Figure 2. CO₂ emission increased significantly after addition of wastewater in both the aerobic and anaerobic samples. CO₂ production was higher in the aerobic soil (average of 160.6 mg/day) than for the anaerobic samples (96.8 and 114.4 mg CO₂ for 0.5 and 0.75 mL/g loadings, respectively). Production did not increase in the aerobic sample between the two loading rates, however, indicating that incorporation of C into microbial cells components is occurring. Likewise, CO₂ emission did not level off significantly during the day. Unlike the breakdown of BOD which occurred over the first 4-8 hours of incubation, release of CO₂ continued over the entire incubation period.

In summary, this experiment demonstrates the rapid decrease in BOD when soil conditions remain aerobic. The rate of BOD breakdown demonstrated here is probably an upper limit on the actual rate in the system because the microcosms are completely stirred reactors. Addition of wastewater rapidly increases the microbial population, as indicated by CO₂ evolution. The stimulation is greater under aerobic conditions. Potential problems when anaerobic conditions develop in the system have also been seen in this study.

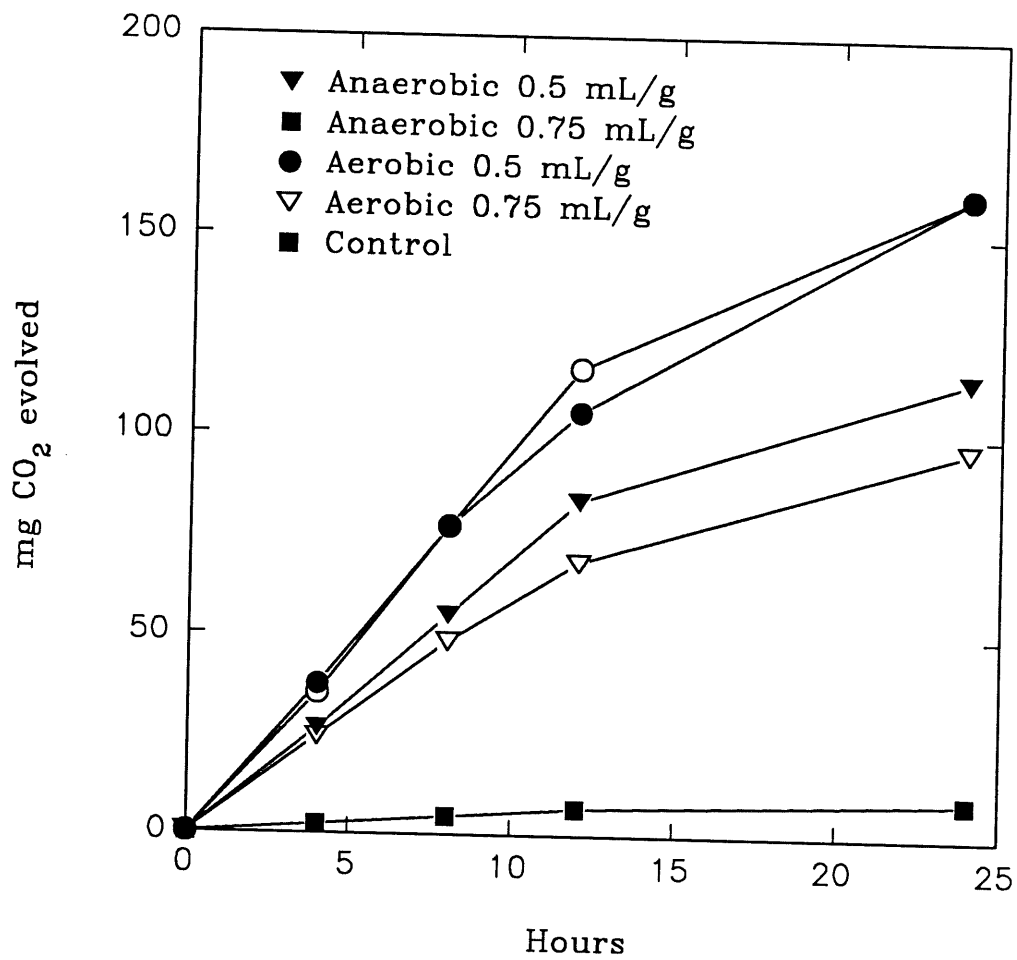


Figure 2. Evolution of CO₂ from controlled microcosms after addition of various amounts of alligator farm wastewater.

4. Design and scale-up of soil biofilter system

Introduction

Criteria exist for the scale-up and design of functional land application systems including overland flow systems. These design procedures have been developed for the treatment of municipal wastewaters although it is likely that many of the same principles would apply to high BOD industrial wastewaters. The guidelines in widest use are from the "Process Design Manual for Land Treatment of Municipal Wastewater (US EPA, 1981) and the supplement to this manual (US EPA, 1985). The original manual outlined primarily empirical methods of designing the size, operating principles, and apparatus required for the three most common types of land application systems: overland flow, rapid infiltration and slow rate systems. Subsequent investigations have shown that the empirical method results in systems that have more application area than is necessary for secondary treatment of municipal wastewater (Witherow and Bledsoe, 1986; Martel et al., 1982). This has led to the development of a rational, non-empirical design procedures for land application systems (Martel et al., 1982). These design procedures were incorporated into a supplement to the original EPA design manual (US EPA, 1985) and have been used in the design of full-scale land application systems since that time.

The procedures used for design of municipal overland flow systems will be summarized below. This general design procedure will be used to scale a working system for the alligator farm wastewater investigated previously. Systems will be designed for conditions where discharge limits on either BOD, N or P are the controlling factor.

Rational design procedure for overland flow systems

The rational design procedures summarized below are based on knowledge of the two general concepts: a). the relationship between wastewater application rate and detention time of wastewater on the slope and b). the relationship between the detention time and the removal of BOD, N and P in the system. In simple terms, the wastewater application must be low enough so that the water will remain in contact with the soil a sufficient period of time to reduce pollutants to desired levels. These concepts will be particularly important for high BOD wastes which will require longer detention times to reduce contaminants to desired levels.

Two similar design models have been developed to determine land application areas to meet specific discharge limitations (Witherow and Bledsoe, 1986). These are:

$$C_S/C_O = A \cdot \exp[(-k \cdot S)/(q^n)] \quad (1)$$

$$M_S/M_O = A \cdot \exp[(-k \cdot S)/(G^{1/3} \cdot q_{avg})] \quad (2)$$

where C_S = pollutant concentration at a distance downslope S , in mg/L

C_O = initial pollutant concentration, mg/L

A = constant

k = rate coefficient, m/h

S = distance downslope, m

q = applied wastewater rate $m^3/m \cdot h$

n = constant

M_S = mass of pollutant at distance downslope, S , kg

M_O = mass of pollutant at initial point

q_{avg} = average of applied and discharged wastewater,

G = slope grade, m/m.

The total application area can be computed from parameters determined in 1). and 2). using the equation:

$$\text{area} = QS/qP \quad (3)$$

where Q = average daily flow, m^3/d

P = application period, h/d

q and S are determined from equations 1) and 2).

These equations form the basis of the design process although complicated equations such as 1). and 2). do not need to be solved for each system. A series of curves have been developed from these models for BOD, N and P removal from data obtained at working overland flow systems treating municipal wastes. Unfortunately, it is doubtful if these empirical data from municipal wastewater systems will be applicable to high

BOD wastewaters such as that from the alligator farm. Therefore, data obtained from the present study were used to design the system.

A slightly modified design procedure has been proposed by Martel et al. (1982). This method involves the important concept of the hydraulic detention time. The design procedure involves three steps: 1). Determining the detention time required for the limiting pollutant of interest to be removed below the discharge criteria (This can be estimated from graphs such as Figure 1), 2). Calculating the application rate necessary to meet this detention time (this is accomplished through hydraulic considerations) and 3). Calculating the land area necessary for the treatment system. Since detention time was determined for the application rates used in these experiments this method will be used to design a hypothetical system for the alligator farm wastewater.

System design example

An example design calculation is presented below and is summarized in Table 1. An alligator farm containing 2000 animals produces wastewater at a rate of 2 gallons per animal per day (4000 gpd=15.1 m³/day). The farm operates year round and has a lagoon which can serve as a holding pond on days when wastewater is not applied to the system. The average pollutant content of the wastewater is: BOD₅=400 mg/L, NH₄⁺=75 mg/L, organic N=75 mg/L and P=10 mg/L. The hypothetical discharge limits on the facility will be 30 mg/L BOD, 20 mg/L for each ammonia-N and organic-N, and 5 mg/L for P. The run-off fraction of the wastewater applied will be 0.8, because of the slow permeability of the soil and the slow evaporation in the humid Louisiana climate. The % mass removals for BOD, organic-N, ammonia-N and P can be calculated as:

$$\% \text{ removed} = \frac{(1.0 * \text{influent concentration}) - (\text{run-off fraction} * \text{discharge limit})}{1.0 * \text{influent concentration}} * 100 \quad (3)$$

Calculations for these pollutants results in BOD removal (94%), ammonia and organic N (79%) and P (60%). In Figure 1, loading kinetic data presented earlier in the report are summarized. From this graph detention times necessary to meet the discharge criteria are:

BOD (188 minutes), ammonia-N (68 minutes), organic-N (54 minutes) and P (115 minutes). Therefore, BOD is the limiting pollutant and the design will be based on a detention time of 188 (approximately 190) minutes.

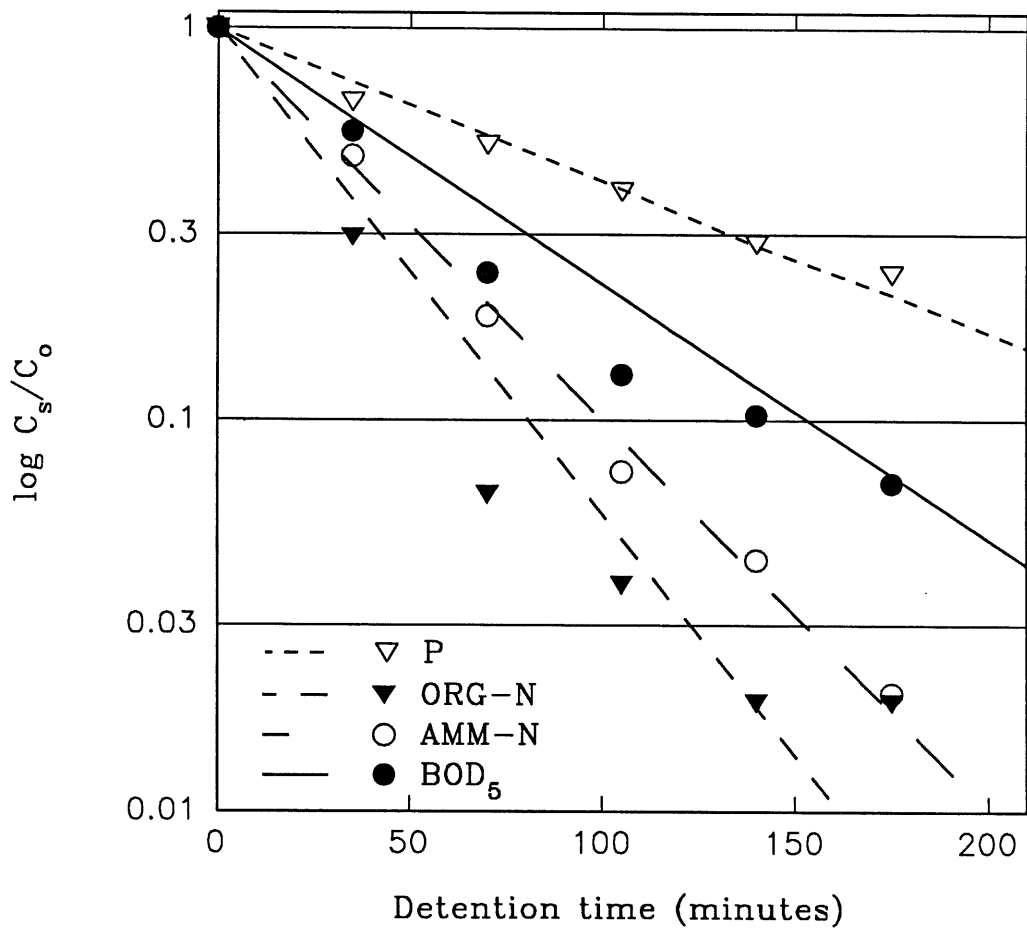


Figure 1. Summary of removal rate data for phosphorus (P), organic N (ORG-N), ammonia-N (AMM-N) and BOD (BOD₅) in land application system at a 1 cm/day loading rate.

Assuming the topography of the site will allow a slope 50 m in length with a slope of 2% then the allowable application rate can be calculated from the equation below (Martel et al., 1982):

$$q = 0.078 * L / ((S)^{1/3} * T) \quad \text{where } q < 0.2 / S^{1/3} \text{ to prevent scour} \quad (4)$$

where q = overland flow rate $m^3 \cdot m^{-1} \cdot hr^{-1}$

L = slope length, m

S = slope, m/m

T = detention time, minutes

For this system:

$$q = 0.078 * 50 / (0.02)^{1/3} * (190 \text{ min.}) = 0.076 \text{ m}^3 \cdot \text{hr}^{-1} \cdot \text{m}^{-1}$$

Assuming wastewater can be applied for 10 months a year (40 weeks) for 10 hours daily for 5 days per week, annual application time is 2000 hours. The annual application rate, Q_a , can be calculated from the following equation (Martel et al., 1982):

$$Q_a = q * y / r \quad (5)$$

where r = overland flow coefficient = $(1.0 + \text{runoff fraction}) / 2 = 0.9$

y = operating time per year, 2000 hr/yr.

For this system:

$$Q_a = (0.076) * 2000 / 0.9 = 168.9 \text{ m}^3 \cdot \text{yr}^{-1} \cdot \text{m}^{-1}$$

The annual design flow = $15.1 \text{ m}^3/\text{day} * 365 \text{ days} = 5500 \text{ m}^3/\text{year}$. Assuming an additional $500 \text{ m}^3/\text{year}$ from precipitation accumulating in the lagoon and the total wastewater applied to the site for the year will be $6000 \text{ m}^3/\text{year}$. The annual application rate, Q_a has been calculated as $168.9 \text{ m}^3 \cdot \text{yr}^{-1} \cdot \text{m}^{-1}$, the total width needed for treatment is $6000 \text{ m}^3 \cdot \text{yr}^{-1} / 168.9 \text{ m}^3 \cdot \text{yr}^{-1} \cdot \text{m}^{-1} = 36 \text{ m}$. Therefore, an application area of $36 \text{ m width} * 50 \text{ m length} = 1800 \text{ m}^2 = 0.18 \text{ ha}$.

In summary, the rational design procedure has been used to size an overland flow system for a hypothetical alligator farm. The relatively small area required (0.18 ha=approximately 1/2 acre) demonstrates the applicability of this treatment technique to this waste stream. Also, the dimensions of the system can be easily recalculated depending on the topography of the site or any other changes in the volume produced, etc. Another advantage of this system is that it can easily be added on to the most common existing system, the oxidation lagoon. Lagoon could serve as a holding pond to equalize the flow onto the land application system, storing precipitation, and providing a measure of pretreatment for the BOD in the raw wastewater. Wastewater could be pumped from the lagoon to the top of the slope or, if topography allowed, a passive run-off system could be used to transfer wastewater to the slope when the holding lagoon filled up.

Table 1. Design of soil biofilter system for alligator farm wastewater.

A. System characteristics:

- a). Influent BOD₅ (C₀): 400 mg/L
- b). Required effluent BOD₅ (C): 30 mg/L
- c). BOD removal is the limiting pollutant requiring detention time of 190 minutes.
- d). Daily wastewater production = 15.1 m³
- e). Yearly wastewater estimate = 5500 m³ + 500 m³ (precipitation)
= 6000 m³.

B. Application rate to satisfy detention requirements:

- a). assuming topography will allow a 50 meter, 2% slope
from equation (4): $q = 0.076 \text{ m}^3 \cdot \text{m}^{-1} \cdot \text{hr}^{-1}$

C. Annual application rate (accounting for winter off periods and percolation losses):

- a). from equation (5): $Q_a = 168.9 \text{ m}^3 \cdot \text{yr}^{-1} \cdot \text{m}^{-1}$

D. Area required = yearly design flow/yearly design application rate

- a). Yearly design flow = 6000 m³/year
Yearly application rate = 168.9 m³/year·m
Width required = 6000/168.9 = 36 m
- b). Total area required = 50 m * 36 m = 1800 m² = 0.18 ha

Conclusions and Recommendations

This study has demonstrated the feasibility of overland flow treatment of wastewater from two Louisiana industries, alligator farm wastewater and sugar refinery wastewater, in laboratory-scale treatment systems. Treatment of BOD in the soil biofilter system was demonstrated in these experiments (94% of the BOD in the sugar refinery canal wastewater and 64% of the alligator farm wastewater BOD was removed at a loading rate of 1 cm/day). In addition, the optimal detention time was determined for reducing the BOD in the alligator wastewater below secondary treatment standards (approximately 190 minutes). Removal of N from the alligator wastewater was very efficient with a 95% removal requiring a detention time of 150 minutes. Removal of P was less efficient due to the anionic form of this pollutant. The P capacity of the soil biofilter was estimated using P adsorption isotherms. Calculation of P retention showed a limited ability of the system to adsorb P (< 10 years). Scale-up of the system for a working alligator farm was also performed based on current EPA design practices. An overland flow system with a land area of around 1/2 acre would be needed to treat wastewater from an alligator farm with 2000 animals.

Further study at the pilot plant scale is necessary to demonstrate treatment under field conditions. This treatment system has the ability to prevent surface and groundwater pollution from untreated or partially treated wastewater. Further development of the system to these industries should be pursued as a cost-effective, efficient method of treating these wastewaters.

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