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Ball Powder Production Wastewater Biological Treatability Studies

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Ball Powder (BP), a smokeless double-based propellant, is manufactured at Badger Army Ammunition Plant (BAAP), Baraboo, Wisconsin. The full-scale manufacture of this propellant produces a multicomponent wastewater containing NG (nitroglycerin), NC (nitrocellulose), EA (ethyl acetate), DBP (dibutylphthalate), DPA (diphenylamine), and 2-N-DPA (n-nitrosodiphenylamine). The last three compounds are categorized as EPA priority pollutants. In addition, NG, DBP, DPA, and 2-N-DPA are toxic and consequently limited to detection limits in the proposed Wisconsin Department of Natural Resources (WDNR) limits. Presently in a caretaker status, mobilization plans require that BAAP be capable of treating its wastewater prior to discharge, in the event of activation. In anticipation of possible renewed production activity, process wastewater (WW) treatment facilities are being modernized. An earlier study (contract No. DAAK 11-SS-D-0008) conducted on BP wastewater at BAAP reported that NG adversely impacted biological treatment processes resulting in an unacceptable system performance in terms of effluent BOD, TSS, NG, DPA and 2-N-DPA.

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#19 (continued): Contrary to these findings, amenability of NG to microbial degradation is adequately documented in the literature. Based on available published literature, biodegradability of NG in BP wastewater was jointly re-investigated on a pilot-scale by The University of Connecticut and BAAP (contract No. DAAL03-86-D-0001) in cooperation with USATHAMA at BAAP, Baraboo, WI. Although amenability of NG is documented in the literature, it remains unclear whether NG can serve as a primary carbon source that can support microbial growth. In light of recently reported inhibitory behavior of NG on biochemical transformations [A. D Little, 1989b], the primary objectives of this study focused on (1) assessing, on a pilot-scale biodegradability and fate of NG present in BP production wastewater and its impact on the overall system performance; and, (2) investigating, on a bench-scale, the potential of NG to serve as a primary growth substrate. Secondary objectives included (1) evaluating the suitability of EA as a primary substrate; (2) ascertaining the endogenous denitrification capacity of facultative cultures in batch reactors treating BP production wastewater; (3) evaluating the impact of fill and idle phases on system performance; and, (4) developing a model that enhances SBRs capability in treating toxic wastes in general and NG specifically.

To realize the study objectives, a test scheme comprised of three phases was developed and the testing performed over a period of five months. Phase I: Acclimation of biomass to BP wastewater without NG; Phase II: Acclimation of biological cultures to NG; and Phase III: Evaluation of system performance with actual process wastewater as expected during full-scale operation. A pilot-scale BP manufacturing plant produced wastewater that was completely consistent with the actual production wastewater. During the first two phases of the study, BP was manufactured without the use of NG so that the biological cultures could be first acclimated to the background wastewater and subsequently to NG. Acclimation of biomass was done by augmenting NG concentrations in the feed in steps ranging from 3 to 40 mg/L. In order to maintain a influent COD/NG $\geq$ 10 (a ratio based on an earlier study to insure stable operation) and a feed of consistent strength, EA was spiked as required. Sludge wasting was done on a periodic basis to maintain a F:M ratio of approximately 0.15 through the study.

Results: Contrary to the previous findings, the results of the pilot-scale study demonstrated that under proper acclimation and suitable COD/NG ratio, NG is biodegradable with no deleterious impacts on the overall system performance. In the operating concentrations of approximately 200 mg/L, NG was consistently removed to below detection limits. Degradation of NG took place primarily under aerobic conditions when the biomass was actively metabolizing the growth substrate. NG was found not to be toxic and exhibited no adverse impacts either on the removal of priority pollutants or in meeting the effluent standards. Priority pollutants were consistently below detection limits and exhibited no variations due to F:M ratio fluctuations as reported previously. Failure of NG to undergo degradation when supplied as sole carbon source indicated that it behaves as a non-growth substrate. However, its removal in the presence of alternate growth substrates in the pilot study suggested that NG undergoes a co-metabolic degradation. Consequently, in order to realize a stable system performance, the influent BOD must be supplemented externally with sufficient suitable growth substrate. The obligate presence of EA, the growth substrate, required during the transformation of NG, the co-metabolite, was insured under aerobic conditions. Loss of EA due to volatilization was found to be minimal.

SBR system was able to consistently meet the proposed NPDES effluent criteria and exhibited no operational and maintenance difficulties at any stage. The SBR system proved to be a viable treatment option for biological oxidation, nitrification, and denitrification in a single unit. In spite of being a combined system, no difficulty was encountered in meeting effluent suspended solids standards. The SBR cycle operated with longer fill and shorter idle phases showed relatively superior quality. Results of concentration-time profiles on the reactor NO_3-N and NG indicated that the lengths of aerobic (8 hrs) and anoxic (5 hrs) selected are appropriate for the operating NG concentrations. No external carbon source was provided during the anoxic phase and NO_3-N was removed to below detection limits by exploiting the endogenous carbon capacity of the biomass.Since a strict static-fill phase in SBRs limits the volume of the waste to be treated per cycle to the threshold toxicity limit, a model has been proposed to alleviate this shortcoming. Model simulations run to investigate SBR response to transient toxic load conditions indicated that approximately 63% decrease in the total cycle time can be achieved in treating a given volume of waste through treatment optimization

BALL POWDER PRODUCTION WASTEWATER
BIOLOGICAL TREATABILITY STUDIES

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Executive Summary

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1. Introduction/Background

1.1 Problem Addressed

Badger Army Ammunition Plant (BAAP), in Baraboo, Wisconsin, a government facility operated by Olin Corporation, is one of two plants and the only military installation that manufactures Ball Powder (BP) Propellant in the United States. During recent years, BAAP has been in a state of lay-away and therefore, no facility presently exists for treating wastewater generated if the plant were to resume operation. In the past, the wastewater generated from the production areas at BAAP was neutralized when necessary, combined, and then fed into a general purpose sewer. From the sewer, the water was then directed to a series of unlined drainage ditches and settling ponds prior to its ultimate discharge at the plant's southern boundary into Grubers Grove Bay on the Wisconsin River [1].

In anticipation of possible renewed production activity, process wastewater treatment facilities are being modernized. But, due to the present caretaker status, there is no NPDES permit if the plant were to renew its production activity. As a result, a consensus has been reached between BAAP, United States Army Toxic and Hazardous Materials Agency (USATHAMA), and Wisconsin Department of Natural Resources (WDNR) to adopt a building block approach for the treatment and effluent criteria for future generated wastewater [1]. According to the "Building Block" concept, the wastewater from the individual production areas would be treated separately, thus, allowing each area to operate independently of the others. With the wastewater from each area being treated separately, the flow rates and the composition of the wastewater generated during the production of ball powder can be predicted (Table 1.1) from BAAP's material balances. An actual characterization of the wastewater generated from the

Table 1.1: Wastewater Composition of Individual Streams from Ball powder Production

	Composition (mg/L)		
Constituent	**Single Base Clarifier**	**Double Base Clarifier**	**Combined**
Powder	280	1220	400
EA	170	235	175
NG	--	60	8
Collagen	180	400	210
Chalk	30	--	30
Sodium Sulfate	2090	--	1770
Sulfate	1410	--	1200
DPA	10	--	10
DBP	--	15	2

EA -- Ethyl Acetate
NG -- Nitroglycerin
DPA -- Diphenylamine
DBP -- Dibutylpthalate

Table 1.2: Proposed WDNR Effluent Limits

Parameter	Limit
pH	6 - 9
BOD	30 mg/L Avg.; 45 mg/L Daily
Nitrate-Nitrogen	50 mg/L
Sulfate	No Limit Assumed
Total Pthalates	5 ug/L*
Total Nitrosoamines	5 ug/L*
Nitroglycerin	5 ug/L*
Total Suspended Solids	50 mg/L
Total Dissolved Solids	No Limit Assumed
Dissolved Oxygen	6 - 8 mg/L

*Detection Limits

Ball Powder pilot plant is presented in section 4 (Table 4.1). The estimated effluent discharge limitations which would have to be met by Badger AAP in the event operations were to be resumed are presented in Table 1.2. The work presented herein is an extension of previous work [1, 2] that evaluated the biodegradability of BP waste streams. Pertinent background information is first reviewed. The objectives of the study and study protocol are then presented in light of previous work and biochemical properties of wastewater constituents. Finally results are presented and discussed with a view towards optimum treatment performance.

1.2 Prior Investigative Work

Studies on the treatability of Ball Powder propellant wastewater were initially investigated in two phases by A.D. Little Inc. [1] under contract # DAAK 11-SS-D-0008. In their first phase of investigation, A.D. Little Inc. [1] conducted both pilot and laboratory bench scale studies to explore the amenability of BP wastewater to biodegradation. The wastewater for the pilot scale studies which is consistent with the actual production wastewater was generated from a pilot scale BP manufacturing unit. The initial estimate of wastewater composition of individual streams from ball powder production is shown in Table 1.1. From this table, the anticipated concentration of NG was reported to be 8 mg/L. The wastewater used in their first phase of investigation was consistent with the full scale production wastewater but devoid of NG. The reason for omitting NG was to facilitate the air transport of wastewater samples to EPA certified laboratories since it was believed that the omission of small amounts of NG (8 mg/L) from the wastewater would not change the toxicity of the wastewater. Two reactor configurations, sequencing batch reactor (SBR), and extended aeration systems were studied as feasible treatment technologies for the treatment of BP wastewater. Both the SBR and extended aeration systems were found to be capable of meeting NDPES effluent requirements (given in Table 1.2) in terms of

effluent BOD, TSS, and NO_3-N, including removing priority pollutants (such as NDPA and DBP) to below EPA detection limits. It was also reported that BP wastewater exhibited no toxic effect on the biomass during the first phase of pilot operation. In terms of overall process efficiency, SBRs proved relatively superior to extended aeration process in treating BP wastewater.

Near the conclusion of the initial pilot study, BAAP expressed a concern that the NG concentration of 8 mg/L reported in the Point Source Survey might be as much as 20 times lower than the actual concentration. Actual characterization of BP wastewater stream showed an average NG inlet concentration of 192 mg/L. In order to facilitate the implementation of a full-scale system, an additional phase of testing with NG was subsequently conducted. Based on pilot scale test results, A.D. Little Inc.[2] concluded that NG in BP wastewater exhibited toxic effects on the biomass; and, therefore, neither system (extended aeration or SBR) was able to consistently meet proposed NPDES effluent limits. Their findings are summarized as a follows.

NG in the range of 150 to 200 mg/L exhibited toxic effects on the biomass causing the following problems:

- Decreased removal of BOD
- Inability to degrade NG and NDPA
- High TSS in the effluent; and
- Steady decrease in MLVSS

In addition, they also recommended that the BP wastewater be pretreated to remove NG prior to biological treatment, most likely by alkaline hydrolysis.

1.3 Previous Studies on NG Biodegradation

Contrary to these findings, amenability of NG to microbial degradation has been documented in the literature. Wendt *et al.* [34], observed NG to be readily convertible to glycerol and nitrite under aerobic conditions in the presence of glucose. Little or no reduction in NG concentration was reported in controls containing no glucose. In another study by Radford Army Ammunition Plant (RAAP) [29], near total removal of NG was reported when COD to NG ratio of ≥ 7 was maintained. In this study, significant variation in the removal efficiency of NG was observed when the ratios of concentration of COD to NG was altered. The results of the RAAP study [29] implied that sufficient amounts of a growth substrate, represented as COD, was necessary to effect the transformation of NG. In mammalian systems, Needleman and Harkey [20] reported NG metabolism in perfused rat livers to be directly dependent on the endogenous glutathione (GSH) reserves. A glutathione dependent enzyme was observed to be responsible for NG metabolism. In essence, failure to undergo degradation in absence of glucose [34] and the dependence of degradation on alternate carbon sources exhibited in other studies [20, 29], suggests that the transformation of NG is dependent on the availability of external growth substrates. Such behavior of certain compounds to biodegradation is not uncommon and had been observed in numerous instances in the past on a variety of compounds. For example, Novick and Alexander [23] observed that the presence of glucose increased the rate of propachlor metabolism, an unsuitable carbon and energy source, in sewage and in pure culture. The rate of metabolism of DDT, a persistent pesticide in the environment, has also been reported to increase with the increasing concentration of glucose in a study by Pfaender and Alexander [26]. Recently, biodegradation of TCE, a prevalent groundwater pollutant, has been reported possible with the methanotrophic bacteria in presence of methane acting as a growth substrate [12, 35]. The behavior of NG to biodegradation is closely parallel to the compounds that exhibit the need for the presence of another growth

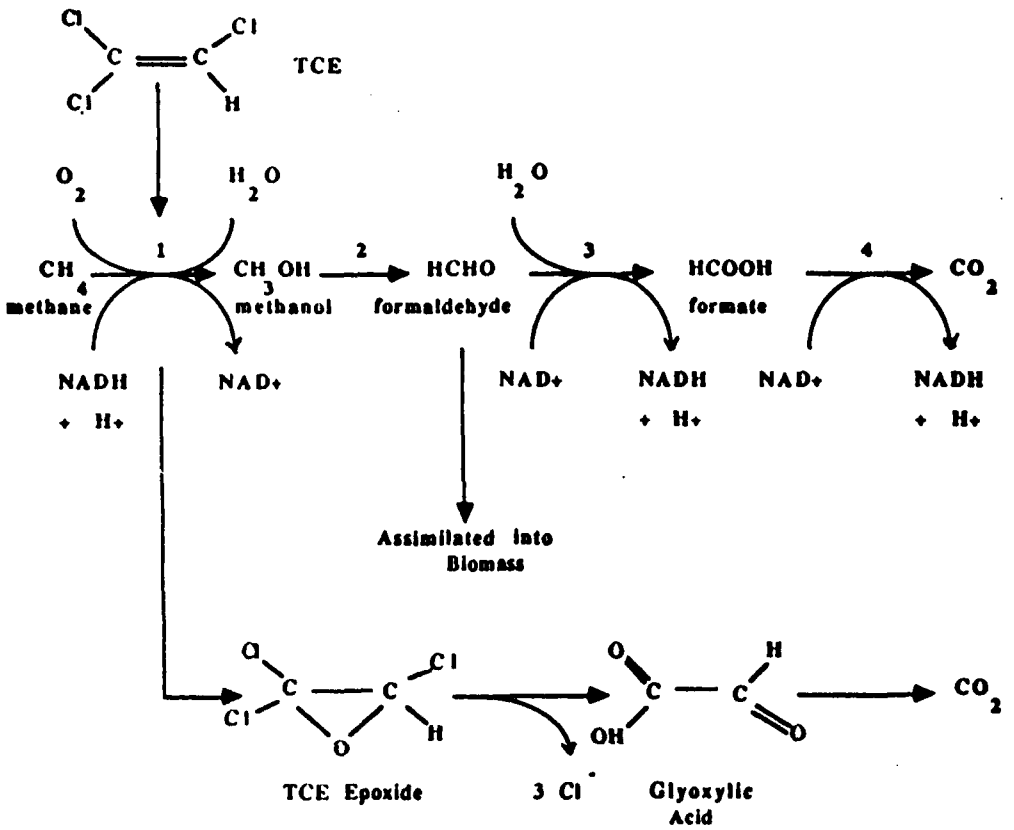
substrate in the medium for their transformation. The degradation of organic compounds that require the obligate presence of growth substrates has been reported to occur through "co-metabolism". Because, such organic compounds, widely known as non-growth substrates, are incapable of supporting microbial growth and therefore their degradation or transformation can only take place when other growth supporting substrates are available for the survival of bacteria.

1.4 Co-Metabolism

1.4.1 Metabolism of Organic Compounds

Organic compounds are broadly classified as biogenic or xenobiotic based on their origin. Biogenic compounds are naturally occurring organic compounds while xenobiotic compounds are the synthetically prepared organic substances. Organic compounds whether biogenic or xenobiotic that can be attacked by micro-organisms and, subsequently be utilized for energy and carbon needs are called primary or growth substrates. Growth substrates therefore furnish the necessary carbon and energy requirements for maintenance, growth, and proliferation of microbial cells. In contrast, certain organic compounds, although susceptible to microbial attack and subsequent mineralization or transformation, that cannot serve the energy and carbon needs of microorganisms are called non-growth substrates. The mechanism by which transformation of non-growth substrates takes place has been referred to "co-metabolism". Recently, co-metabolism has been defined as the transformation of non-growth substrate in the obligate presence of a growth substrate or another transformable compound [8]. A non-growth substrate could be incorporated into cellular components but does not support cellular division and hence cannot serve as the sole source of carbon and energy.

Fig. 1.1: Mechanism of Co-Metabolism



Co-Metabolism of TCE in presence of methane. Enzymes involved: (1) methane monooxygenase; (2) methanol dehydrogenase; (3) formaldehyde dehydrogenase; (4) formate dehydrogenase. Adapted from Dalton and Stirling (1984) and Little *et al.* (1988).

Metabolism of organic substrates in a microbial cell typically takes place through a series of enzymatically catalyzed reactions in such a way that the product of first reaction becomes the substrate for the subsequent enzyme in the degradative pathway. Therefore, an array of enzymes are involved in the catabolism of organic compounds. Products that could not be fitted into any enzyme will accumulate in the system [13]. If certain transformation reactions require energy input in the beginning, a compound will still be able to serve as a growth substrate, if the net energy derived is positive in subsequent degradative steps. Whereas in case of a non-growth substrate, the oxidation state of intermediate products do not allow energy gain by successive oxidative process and hence there seems to be no selective advantage for the micro-organism that converts it [24]. Therefore, a co-metabolite typically requires more energy to be transformed than that which is derived from its transformation reaction, and, as a result, a suitable growth substrate should be present to induce necessary enzymes and yield energy to drive the transformation reaction. The ability of enzymes to modify non-growth substrates manifested in co-metabolism causes energy drain and seems to obscure the metabolic significance of these reactions [8]. The basis for non-growth substrate transformations has been explained in terms of the accidental utilization of existing enzyme system [16, 8, 22]. The enzymes produced as a result of induction due to the presence of growth substrates accidentally attacks non-growth substrate and causes its oxidation simultaneously. The broad substrate specificity or substrate ambiguity of mono or di- oxygenases have been reported to be mostly responsible for initial transformation of co-metabolites [25, 8] This fact that the co-metabolic attack of the non-growth substrate analogs involves same enzymes as that used for oxidation of growth substrates has been recently proved by Nelson *et al.* [22].

1.4.2 Suitability of Growth Substrate

Microorganisms that are capable of degrading a particular non-growth substrate may survive on a variety of growth substrates. But, presence of suitable catabolic substrates is mandatory for the induction of suitable degradative enzymes to effect the transformation of non-growth substrates by co-metabolism. For example, Nelson *et al.* [21] have observed degradation of trichloroethylene (TCE), a non-growth substrate, by a bacterial isolate growing on toluene. However, no degradation of TCE was observed in absence of toluene although the bacterial isolate was growing on a variety of other substrates, thereby indicating the necessity of induction of degradative pathway from a particular substrate. Although there is a need for suitable growth substrate, studies on TCE degradation have demonstrated that there could be more than one degradative pathway, organism, and growth substrate in the environment for the co-metabolic degradation of a particular compound. For example, Little *et al.* [19] observed co-metabolism of TCE with pure cultures of methanotrophs, whereas Nelson *et al.* [22] isolated pure cultures that co-metabolized TCE when induced with toluene. Interestingly in the later case, an aromatic degradative pathway has been implicated in the co-metabolic degradation of TCE. Although NG has been shown to undergo microbial degradation when supplied with either glucose or ethanol as primary substrates in earlier studies [34, 29], EA present in BP wastewater could also be a suitable substrate for NG degradation. This aspect was verified in the present study.

1.4.3 Competitive Inhibition and By-Product Toxicity

As expected in co-metabolism, both the co-metabolite and the growth substrate would be competing for the same enzyme resulting in competitive inhibition. In addition, since non-growth substrate is not a catabolic substrate of the microorganism and its transformation takes place due to the accidental utilization of existing enzyme system, the transformation by-products could be more toxic than the parent molecule. Wackett and Householder [33] have clearly demonstrated with pure culture of toluene degrading bacteria that the intermediate transformation by-products resulting from epoxidation of TCE were more toxic to the cells. Therefore, the transformation capacity of cells is not only a function of the availability of reducing power (growth substrate) but also of the specific co-metabolized compound and toxicity of transformation by-products as well [5]. However, product toxicity can be eliminated or reduced by carefully acclimating and growing a mutualistic microbial consortia that can utilize transformation by-products by other species. Competitive inhibition can be avoided by physically separating reactions using a two stage reactor system as proposed by Alvarez-Cohen *et al.* [5, 6] or by operating the reactor such that critical inhibitory concentrations are not developed in the reactor.

1.4.4 Impact of Insufficient Growth Substrate

Due to the accidental utilization of non-specific enzymes induced by growth substrates, complete transformation capacity of non-growth substrates is realized only when sufficient growth substrates are present to mobilize the required quantities of enzymes. Effect of nutrient addition, as mentioned earlier, on the apparent increase of rate of co-metabolism was studied by Novick and Alexander [23]. Using glucose that can support growth of bacteria which can co-metabolize DDT, Pfaender and Alexander [26] noted that the rate of DDT metabolism increased with the increasing glucose concentration in pure cultures. Similarly, by adding formate, an external reductant, to TCE degrading bacteria, significantly higher removal capacities were observed [5]. As mentioned earlier, NG degradation also showed a strong dependence on external carbon sources. Needleman and Harkey [20] observed the rate and magnitude of NG metabolism in perfused rat livers to be a function of endogenous glutathione reserves. Similarly, results of the RAAP study [29] also exhibited a direct dependence on influent ethanol concentrations for NG degradation. Clearly, concentrations of growth substrate play a significant role in enhancing both the rate and degree of removal of non-growth substrates. However sometimes, due to the natural propensity of microorganism for growth substrate, competitive inhibition may seriously retard the removal of non-growth substrate. Therefore, an understanding of interactions between various substrates is of utmost importance in designing a treatment system.

If degradation of targeted compound occurs by co-metabolism under aerobic conditions, the volatility of growth substrate is of primary concern. Loss of growth substrate due to volatilization may significantly decrease the available growth substrate. As a consequence of volatilization, it would become difficult to maintain the desired amount of growth substrate necessary for the transformation of targeted compound and thereby resulting in poor system performance. In this scenario, not only the biochemical

characteristics but also the physicochemical properties of the growth substrate is of considerable importance for the successful application of co-metabolism for non-growth substrates.

1.4.5 Selection of Microbial Culture

The initial transformation of co-metabolite occurs due to the broad substrate specificity of certain enzymes [22]. The relatively non-specific nature of these enzymes in the catabolic pathway of growth substrate catalyze the conversion of non-growth substrate to a product that may not be a substrate for another enzyme in the organism [8]. As a result, if a compound is co-metabolized by pure cultures the metabolic by-products always accumulate due to the lack of enzymes for subsequent transformations. But if the organism performing the co-metabolism is growing in a mixed microbial community, accumulation of metabolic by-products may not occur because the metabolite could be degraded by another species of organism within the community [28]. The use of mixed culture is preferable when there is a possibility of generation of toxic by-products and also in case of a muticomponent waste. Recently, Little *et al.* [19] have reported that in mixed cultures, heterotrophic bacteria metabolized water soluble TCE breakdown products to a much lower levels than pure cultures due to limited bacterial metabolic activities in the later case. Similarly, Fliermans *et al.* [11] have been successful in oxidizing 99% of exogenous TCE to HCL and CO_2 using mixed microbial cultures.

1.4.6 Possible Causes for Apparent Toxicity of NG

In the light of above discussion on co-metabolism and its related effects and the behavior of NG towards microbial degradation from previous studies, the following were deemed to be the potential possible causes for the apparent persistence/toxicity exhibited by NG in A. D. Little study [2].

- Unsuitability of Ethyl Acetate (EA) for the induction of necessary enzymes to effect the transformation of NG. Because, in earlier studies glucose [34] and ethanol [29] were used as the primary sources of carbon
- Volatilization of EA, the growth substrate, during the transformation of NG under aerobic conditions
- Competitive inhibition from growth substrates
- Production of toxic by-products as a result of co-metabolism
- Toxicity of NG due to its high concentrations in the influent
- Insufficient acclimation of biomass to NG
- Insufficient growth substrate

2. Biological Treatment Systems

2.1 Selection of Treatment System

In the first phase of the study by A. D. Little Inc.[1], when the wastewater did not contain NG, the two candidate technologies, SBR and extended aeration, studied showed that both systems are equally efficient in meeting the NPDES requirements. However SBR systems offer certain advantages over the extended aeration system; the most notable differences being

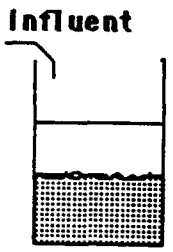
- SBR systems operate without clarifiers
- SBR systems offer greater flexibility in accommodating varying wastewater feed rates
- No returned activated sludge pumping is required, because the mixed liquor is always in the reactor
- SBRs are inherently suitable to the implementation of the aerobic and anoxic conditions in the treatment cycle, if such an operation is warranted

2.2 SBR System/Criteria for Selection

A characterization of BP wastewater (Table 4.2) shows significant amounts of nitrogenous compounds such as nitrocellulose, nitroglycerin, organic nitrogen (TKN), etc in the influent stream. These compounds when degraded under aerobic conditions would generate significant amounts of nitrate-nitrogen as a result of oxidation. For example NG alone in the expected concentrations of 200 mg/L would generate approximately 37 mg/L of nitrate-nitrogen. Wastes of this kind therefore demand a suitable denitrification system in order to meet the effluent criteria in terms of nitrate-nitrogen concentrations. In this situation, SBRs due to their mode of operation are inherently suitable for carrying out

carbon oxidation, nitrification and denitrification in the same reactor utilizing a single facultative biomass. In addition, the A. D. Little Inc.[1] study proved SBRs to be efficient in treating BP wastewater, consistently meeting NPDES limits. Therefore, an SBR system has been adopted for the present study, primarily for the need to include a denitrification phase and for their proven efficiency in treating BP wastewater.

Fig 2.1: Typical Sequencing Batch Reactor (SBR) Cycle



	Operation	
	Air	Mixer
Fill – Add Substrate	On/Off (optional)	On/Off (optional)
React	On (aerobic) Off (anoxic)	On (aerobic) On (anoxic)
Settle – Clarify	Off	Off
Decant – Remove Effluent	Off	Off
Idle – Waste Sludge	On/Off (optional)	On/Off (optional)

2.3 Operation of SBR Systems

A Sequencing Batch Reactor (SBR) is a fill-and-draw activated sludge system typically consisting of four phases: fill, react, settle, draw, and idle. A schematic of a typical SBR operation is shown in Fig 2.1. A cycle for one reactor system consists of all five phases and the cycle time is the total time between the beginning of fill period to the end of idle period. The idle phase, time period between the decant and refilling of reactor, functions as a filler and can be eliminated if not required. Prior to the initiation of the fill phase, the reactor always contains a constant volume of mixed liquor suspended solids typically at concentrations of 10,000 mg/L to 12,000 mg/L. During the fill period the reactor receives the desired volume of waste to be treated in each cycle. The react phase follows the fill phase and is the time period required to complete the desired reactions. The react phase can be divided into aerobic and anoxic react segments depending on whether oxygen/air is supplied or not. During the aerobic react phase both mixing and aeration take place simultaneously. But in the anoxic react phase only mixing occurs, without aeration. In some instances, when fill and react operations are conducted simultaneously, such periods are termed react-fill phases. Periods under which reactors are filled with no mixing and aeration are characterized as static-fill phases. Due to the presence of mixed liquor in the reactor prior to the beginning of fill phases, the influent is diluted after entering the reactor. Therefore, the maximum concentration of the waste occurs in the reactor under static-fill conditions at the end of fill phase. During settle phase, the suspended solids are allowed to settle in the reactor under quiescent conditions with no mixing and aeration. The supernatant effluent is drawn off by gravity during the decant phase through a port located at a desired depth in the reactor.

2.4 Limitation of SBR Systems

Although SBRs offer certain advantages over conventional treatment systems, it is reported in the literature that the sedimentation efficiency of SBRs is impacted by react-fill phase due to the lack of substrate tension. This seriously limits the capability of SBRs in treating wastes that are toxic in nature. Because, if a strict static-fill phase were to be followed, the concentration of toxic waste builds up as the reactor is being filled. As a result, the maximum volume of waste a reactor can receive is limited to the threshold toxicity concentration a biomass can safely tolerate. In order to alleviate this problem a model has been provided in section 7 and computer simulations run to investigate the impact of combined static and react-fill phases.

3. Objectives of the Study

The overall goal of the present study was to treat BP wastewater so as to meet the proposed effluent standards. The primary and secondary objectives were designed to meet this treatment goal . Besides, the objectives were also formulated to acquire a basic understanding of the physicochemical and biochemical properties of the principal constituents of the waste. A knowledge of these properties is essential for the control and optimization of the treatment system design. Section 1.4.6 mentioned a number of possible causes for the apparent toxicity of NG reported in a previous study [2]. Since it was unclear which of these factors were responsible for the observed toxicity, the study objectives, such as acclimation, were designed to explore them in the event of toxicity.

Primary Objectives

- Asses the biodegradability and fate of NG present in BP production wastewater and its impact on overall system performance
- Investigate on a bench-scale the potential of NG to serve as a sole source of carbon and energy.
- Acclimate biomass to NG and determine the threshold limit, if NG exhibits toxicity at any stage of acclimation.

Secondary Objectives

- Evaluate the suitability of ethyl acetate as a primary substrate.
- Explore the fate of NG in the reactor under aerobic and anoxic conditions. And, to evaluate the removal of NG due to biosorption.
- Study the impact of stripping of ethyl acetate, the growth substrate on the removal of NG.
- Investigate the endogenous denitrification capability of biomass.
- Develop a model that enhances the capability of SBRs in treating toxic wastes in general and NG specifically.

Phases of Operation

The study was conducted in three phases.

Phase I: Sludge obtained from a nearby domestic wastewater treatment plant was initially acclimated to BP wastewater without NG. During phases I and II, BP was manufactured without NG so that the biological culture could be slowly acclimated. Phase I was run for approximately 3 weeks to obtain baseline data prior to the introduction of NG into the waste stream. SBR cycle A, shown in Table 5.1 and Fig 5.1, was adopted during this phase.

Phase II: Subsequent to achieving steady-state utilizing BP production wastewater without NG, the culture was acclimated to NG by gradually increasing its concentration in the SBR feed from 2 mg/L to 160 mg/L over 8 weeks (Fig 6.8). The concentration of NG in the feed was augmented in small increments. NG step increases ranged from 3 to 40

mg/L. Approximately 4 to 5 days of acclimation per incremental NG concentration were allowed to insure process stability. Each increase in NG concentration was closely monitored for deterioration in the system performance. There was a lag of more than one week on the results of NG and other priority pollutant assays from the commercial laboratory due to logistical constraints. Consequently, effluent COD (total) was chosen as criteria for evaluating daily system performance. SBR cycle A (Table 5.1) was implemented for the first 4 weeks and cycle B (Table 5.1) for the next 4 weeks of this phase.

Concurrent with phase II, bench-scale studies evaluating the suitability of NG as a sole carbon source were conducted.

Phase III: This phase was operated for approximately 4 weeks. System performance was evaluated with actual process wastewater, where NG was added within the production process. Cycle B (Table 5.1) was adopted for this phase.

4. Wastewater Preparation and Characterization

4.1 Wastewater Preparation and Storage

Wastewater for the pilot scale studies was produced from a pilot scale BP manufacturing plant located on the site. The pilot-scale BP manufacturing plant generated wastewater that was consistent with actual process wastewater*. Wastewater composition generated from the pilot-scale BP manufacturing pilot plant is presented in the Table 4.1. The pilot-scale BP manufacturing plant generated 2270 L (600 gallons) of wastewater per batch every fifteen days: 1135 L (300 gallons) each was generated from coating and hardening operations. Since NG was added during the coating operation, which occurs at the end of the production phase, it was possible to prepare wastewater that was consistent with the original production wastewater without NG. BP wastewater without NG was used during the first two phases of the pilot plant operation. Wastewater without NG was used during phase II of the pilot study (i.e. NG acclimation phase) in order to facilitate controlled addition of NG to the influent feed. Upon completion of production, each batch of wastewater was transferred to a 2270 L (600 gallon) steel tank mounted on a trailer, that was later transported to the pilot-scale wastewater treatment facility. The fortnightly production of wastewater was sufficient to supply the pilot scale treatment system using BP wastewater at a rate of 151 L (40 gallons) per day for fifteen days. Since the wastewater was generated every fifteen days, the composition of the wastewater varied somewhat during the holding period, particularly with respect to COD and BOD. To prevent deterioration over the fifteen day holding period, the wastewater was stored outside in cold weather during winter months. Due to the storage of wastewater in the cold weather, the temperature of the feed occasionally dropped below 0^{o}C. In order to bring the feed to

* Personal communication with G. Shalabi

Table 4.1: Wastewater Composition

Parameter	Avg. Concentration, mg/L
BOD	910
COD	1450
Ethyl Acetate (EA)	343
Nitroglycerin (NG)	180
DBP	1.2
DPA	2.0
2 - nDPA	0.1
Nitrate Nitrogen*	27
Ammonia	10
TKN	70

*Due to NG interference

room temperature, two feed tanks were used alternatively and the standby feed tank was used to store 151 L (40 gallons) of wastewater pumped one day prior to its use. The standby feed tank also served as a point for adjustment for nutrient requirements since the BP wastewater was deficient in certain essential nutrients, especially nitrogen and phosphorous.

4.2 Nutrients

Typical composition of BP wastewater is shown in the Table 4.1. The original BP wastewater when freshly prepared, contained on average 6 mg/l of ammonia-nitrogen and 70 mg/l of total kjeldahl nitrogen (TKN). BP wastewater was deficient in phosphorous. Fresh wastewater had, on average, a total COD of approximately 1500 mg/l and a total BOD of approximately 1000 mg/l (Table 4.1). Inorganic nutrients are required in the proper amounts if organic carbon is to control the rates of substrate removal. The most likely to be deficient are nitrogen and phosphorous. Additionally, these are the two inorganic nutrients required in larger quantities as compared to other nutritional requirements. Microbial cells are approximately 10.5% nitrogen on a dry weight basis. Phosphorous is approximately one fifth of the nitrogen requirement. Nutrients must be added in slight excess of the theoretical amounts to ensure that the carbon concentration is rate limiting. Accounting for growth yield, 7 mg/L of ammonia-nitrogen and 2 mg/L of phosphorous was added per 100 mg/L of BOD, thereby maintaining a ratio of 100:7:2 of BOD:N:P. Nitrogen and phosphorous were added in the form of ammonium chloride and phosphoric acid, respectively. In calculating the amount of ammonium chloride to be added, using the above ratio, TKN present in BP wastewater was ignored due to the uncertainty of its availability to supplement nutrient requirements. Although this approach is on the conservative side of accepted standards, it was adopted to insure safe operation. An effort was made toward the end of the study to optimize nutrient addition.

4.3 Alkalinity

Strongly alkaline or acidic conditions either due to wastewater characteristics or generated as a result of biochemical reactions adversely affects the performance of biological processes. Therefore, it is necessary to adjust the wastewater to a neutral pH by properly buffering it prior to entering the reactor. During the study, the average pH of the reactor was relatively stable and ranged between 6.5 and 7.5 in the beginning. However, once the nitrifying bacteria became established, indicated by decreasing trend in the effluent ammonia-nitrogen concentrations, a significant lowering of pH was observed due to excessive utilization of alkalinity. In order to maintain pH stability during nitrification, alkalinity, in the form of sodium bicarbonate ($NaHCO_3$) was added. Based on the stoichiometric requirements of nitrification by nitrifying bacteria, approximately 8.5 mg of bicarbonate per mg of ammonia-nitrogen was added to supplement the influent.

4.4 Ethyl Acetate

Although efforts were made to preserve the composition of wastewater over the holding periods, significant decreases in the influent COD and BOD were observed which may be due to biodegradation and volatilization of compounds. Ethyl Acetate (EA), a colorless organic liquid, was present in fairly high concentrations in the BP wastewater stream and served as a major source of carbon for the biomass. EA has a vapor pressure of 72.8 mm of Hg and a solubility of 79 g/L at 20 °C [32]. In order to maintain a feed of consistent strength with respect to COD (total), EA was spiked as required to maintain an influent COD(T) of approximately 1500 mg/l. A mass ratio (COD/EA) of 1.55 was adopted for calculations [32]. For the purpose of spiking the required amounts of EA, COD analysis was performed twice every day. The second time COD determination was done to ensure that the final influent attains the required strength in terms of total COD after the addition of EA, which was calculated based on the initial strength of the influent. The

calculated and experimentally determined values were in good agreement. The strength of the influent, initially maintained at approximately 1500 mg/l with respect to COD (total), was subsequently increased to approximately 2000 mg/l as the concentration of NG in the influent increased. This change was necessary in order to maintain COD/NG $\geq$ 10, a ratio decided based on earlier work [29] to ensure safe operation in the event that NG could not support growth.

5. Pilot-Scale Testing

5.1 SBR Operation

Studies on BP wastewater treatment were conducted in a sequencing batch reactor (SBR) system of 379 L (100 gallon) capacity. A computer completely controlled the operation of SBR which required minimum manual supervision. Any combination of fill, react, settle, decant, and idle could be easily programmed using the computer. SBRs have been demonstrated to be suitable for treating batch production wastewater. Batch reactors are inherently suited to achieving carbon oxidation, nitrification and denitrification in a single reactor by using a mixed-culture facultative biomass in alternate aerobic and anoxic cycles [3, 4, 27]. The A. D. Little study [1] found SBRs to be efficient in treating BP wastewater without NG, consistently meeting proposed NPDES requirements. Therefore, an SBR system was adopted for the present study, primarily for the need to include a denitrification phase (Table 4.1). The SBR, feed tank, and effluent tank were housed in a constant-temperature room, thermostatically controlled to an average of 27± 2 °C. Two SBR cycle schemes A and B (Table 5.1) were adopted during various study phases to evaluate the impact of static fill time. All cycles were operated with a static fill phase (Table 5.1) since it was observed early in the study that settling characteristics deteriorated significantly when mixing occurred during this phase. The lengths of aerobic (8 hrs) and anoxic (5 hrs) phases were based on earlier studies [3, 4, 7, 9, 27] and found to be appropriate from the results of subsequent temporal profiles of NG and NO_3-N. Gaseous nitrogen released during denitrification can become entrapped in biomass resulting in poor settling [17]. Consequently nitrogen gas was stripped by mechanical agitation and aeration for 30 min before the biomass was allowed to settle by gravity. Supernatant was drawn off by gravity through a port located approximately 61 cm (2 ft) below liquid surface. The

volumetric feed flow rate was adjusted and maintained using a peristaltic pump so that 151 L (40 gallons) of influent entered the reactor in the specified static fill time. Approximately 60 gallons of mixed liquor remained in the reactor prior to initiation of fill phase, bringing the SBR volume to 379 L (100 gallons) in each cycle (Figs 5.1 and 5.2). A schematic of variations of reactor volume as a function of time for the two cycle schemes is presented in Figs 2.1 and 2.2 . Air was supplied at a rate of 141 L/min (5 ft^3/ min) which insured dissolved oxygen concentration of ≥ 2mg/l throughout the aerobic react phase. Significant changes in operation of SBR cycles from that of earlier work [1] was inclusion of anoxic and N_2 gas stripping phases (Table 5.1).

Table 5.1: SBR Cycle Schemes A and B

Phase	Time, Hr.		Operation
	Scheme A	Scheme B	
Static Fill	2.5	4	Blower, Mixer off
Aerobic	8	8	Blower, Mixer on
Anoxic	5	5	Blower off, Mixer on
Stripping of N2 Gas	0.5	0.5	Blower, Mixer on
Settle	1.5	1.5	Blower, Mixer off
Decant	0.75	0.75	Blower, Mixer off
Idle	5.75	4.25	Blower, Mixer off

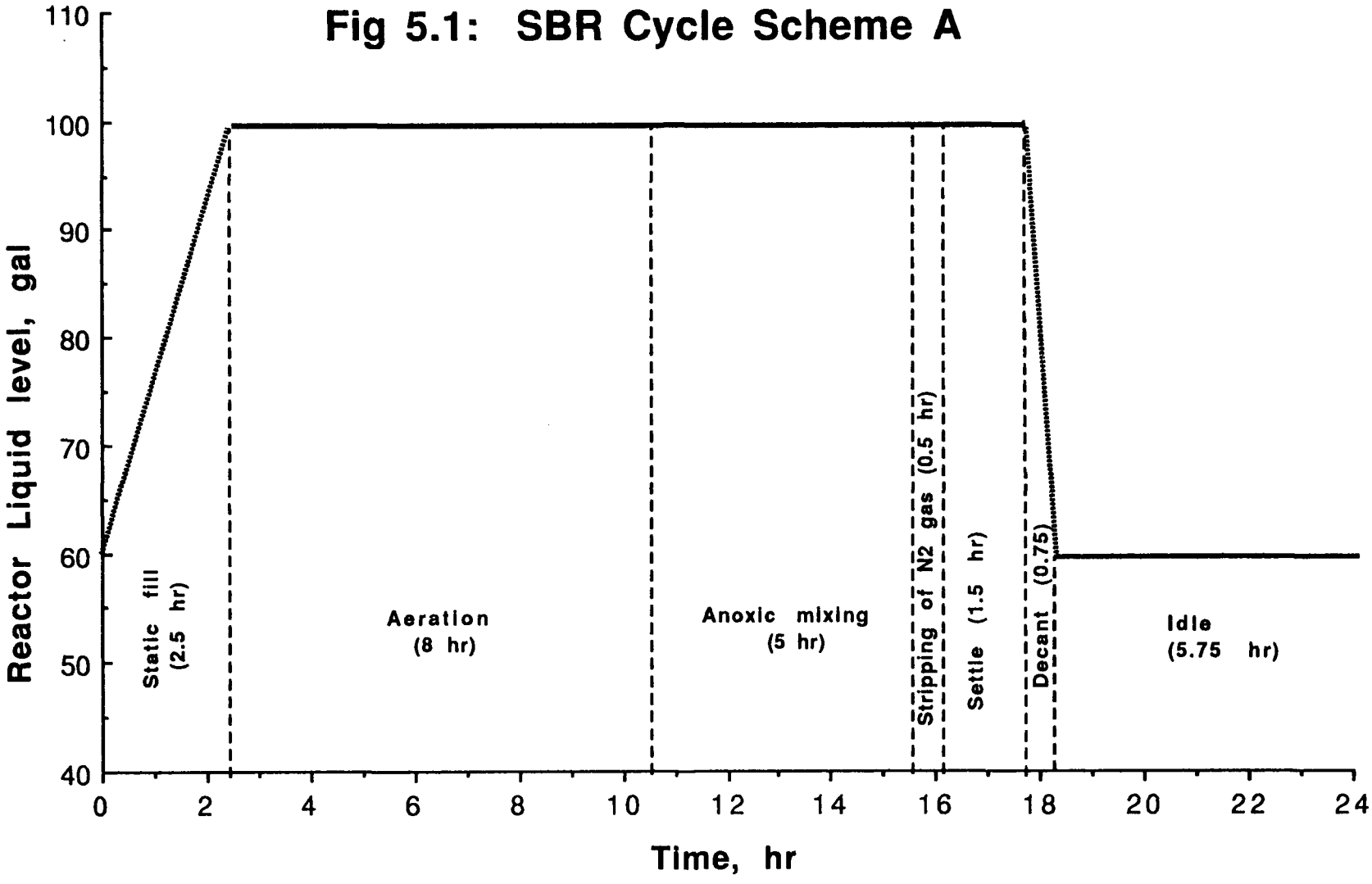


Fig 5.1: SBR Cycle Scheme A
Reactor Liquid level, gal
110
100
90
80
70
60
50
40
0
2
4
6
8
10
12
14
16
18
20
22
24
Time, hr
Static fill (2.5 hr)
Aeration (8 hr)
Anoxic mixing (5 hr)
Stripping of N2 gas (0.5 hr)
Settle (1.5 hr)
Decant (0.75)
Idle (5.75 hr)

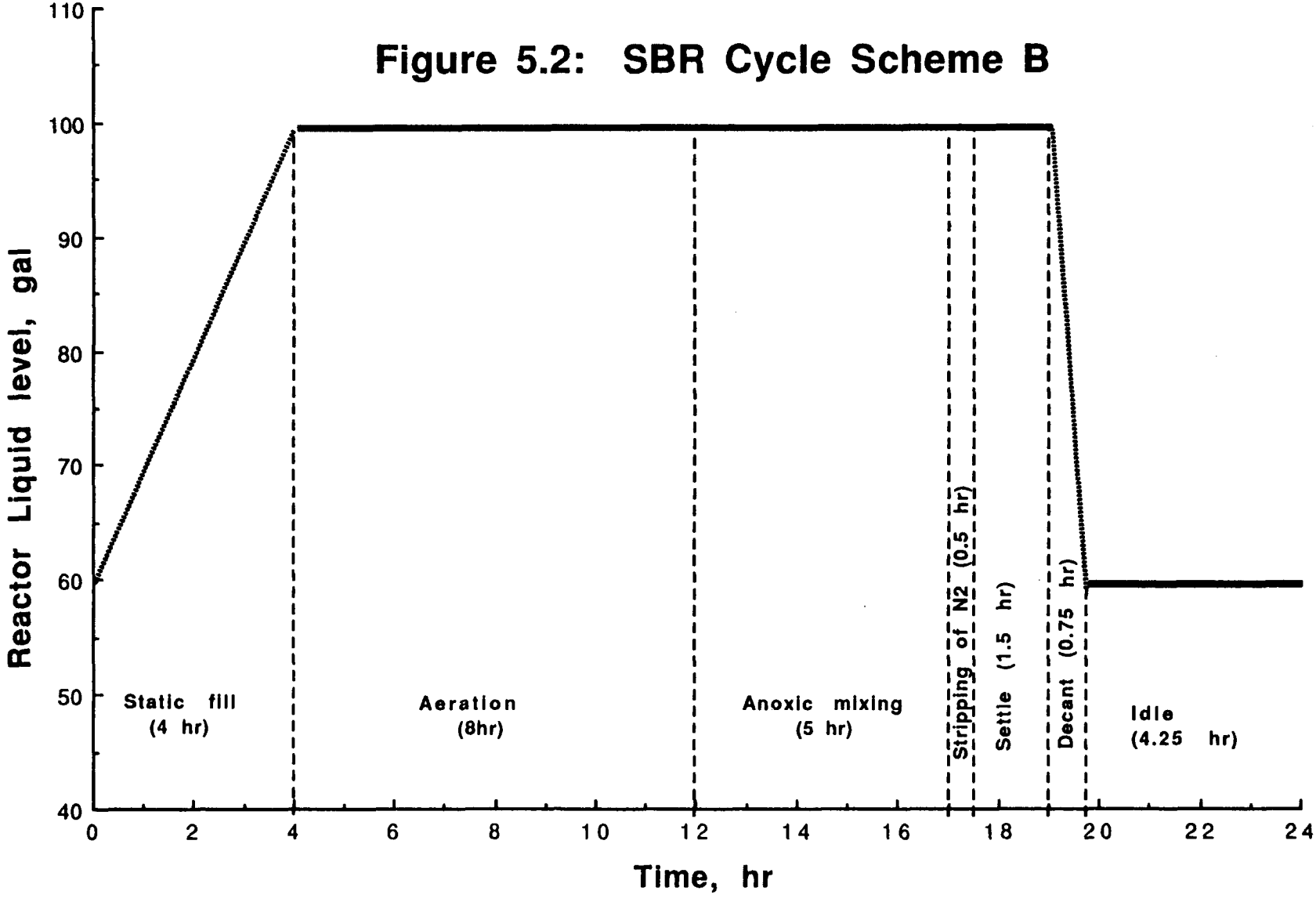


Figure 5.2: SBR Cycle Scheme B

5.2 Start-Up of Biological Reactors

For the operation and control of activated sludge systems, F:M (Food to Microorganisms) ratio is one of the most widely used empirical relation. F:M is defined as the ratio of total mass of substrate supplied (mg/L of COD times influent volume) to total mass of microorganisms (mg/L of biomass times volume of mixed liquor). Based on the values reported in the literature [10], an average F:M ratio of 0.15 was maintained throughout the study. Since it was reported in the earlier study [1] that BP wastewater without NG is not toxic to bacteria and required no acclimation period, a concentrated biomass from the Baraboo Municipal Sewage Treatment Plant was directly added to the raw wastewater. This allowed reactors to start with a MLVSS concentration of approximately 3000 mg/L. Because, the influent total COD was maintained initially at approximately 1500 mg/L , the concentration of the biomass (MLVSS) was allowed to increase up to approximately 4000 mg/L and maintained at this level. The strength of the influent, initially maintained at 1500 mg/l with respect to COD (total), was subsequently increased to 2000 mg/l as the concentration of NG in the influent increased. In order to maintain a constant F:M ratio for all phases, biomass concentration was allowed to increase proportionally as influent COD (total) increased. A layer of dead biomass was found floating soon after the reactor was seeded. The dead mass of bacteria floating on the surface of the reactor was skimmed off on a daily basis. The quantities of floating dead biomass steadily decreased and virtually no dead biomass was found on the surface of the settled waters in the reactor after fifteen days. Once the required concentration of biomass in the reactor was achieved, sludge was wasted at periodic intervals to maintain a constant F:M ratio. Sludge wasting was accomplished by drawing off approximate amounts of mixed liquor during N_2 gas stripping phase. The exact amounts of sludge to be wasted was calculated after the MLVSS of the reactor was determined in the laboratory. The

excess sludge (beyond experimentally determined) was added back to the reactor before the start of fill phase.

5.3 Acclimation of Biomass to NG

Subsequent to achieving system steady state utilizing the BP wastewater without NG, the culture was acclimated to NG through periodic synthetic incremental additions. NG acclimation was carried out in phase II where it was added to the influent up to the expected real process wastewater concentrations (160 mg/l). NG step increases ranged from 3 to 40 mg/l. Approximately 4 to 5 days of acclimation per incremental NG concentration were allowed to insure process stability. Each increase in NG concentration was closely monitored for any deterioration in the system performance. Since there was a lag of more than one week on the results of NG and other priority pollutant assays, effluent COD (total) was chosen as criteria for evaluating daily system performance. This approach necessitated steady increases in influent NG concentrations.

NG, in addition to being a sensitive explosive, is a hydrophobic substance with a moderately low solubility of 1.8 g/L at 20 °C [32]. During the earlier stages of NG acclimation phase, appropriate amounts of NG/EA mixture were directly added to 2270 L (600 gallon) feed tanks containing 151 L (40 gallons) of feed. The contents of the tank were then mixed by circulating the wastewater using a pneumatic pump. But, due to the large surface area of 2270 L (600 gallon) feed tanks, the mixing device was inefficient causing incomplete dissolution of NG. As a result, the measured NG concentrations were much less than the actual concentrations. In addition, the 6 to 8 hours of mixing of influent required for dissolution of NG in the large feed tanks caused losses of EA resulting in significant lowering of influent COD. To avoid these problems, the required quantities of NG/EA mixture were first completely dissolved in BP wastewater in 5 liter flasks in the

laboratory and the homogeneous solution of NG was added to 151 L (40 gallon) influent. This practice ensured complete dissolution of NG in the influent before entering the reactor. Because of its extremely sensitive nature, NG is stored dissolved in EA and a DBP stabilizer. Therefore, NG used during acclimation was available dissolved in 50% EA by weight. Since EA was present in high concentrations in the wastewater, small additions of it along with NG to the feed did not alter the composition of the wastewater.

5.4 Sampling and Analysis

Sampling frequency, type, and location are outlined in Table 5.2. All samples for traditional analysis were collected, preserved and analyzed in accordance with the Standard Methods [30] at BAAP laboratories. NG, DPA, DBP and 2-N-DPA were assayed, in accordance with EPA Methods, by Hazelton Laboratories, Madison, Wisconsin, using solvent extraction and reverse phase isocratic high performance liquid chromatography [2]. Extraction efficiencies for aqueous and sludge samples for NG were 90% (± 17) and 70% (±14), respectively. Since there was a time difference of 24 hours between the influent and effluent sample collections for the analysis of priority pollutants and NG, influent was stored at 4 °C and transported with the effluent and the sludge samples.

Table 5.2: Schedule of Analysis

Parameter	Location		
	Influent	Reactor	Effluent
pH	Daily	-	Daily
BOD (soluble & tota	Daily	-	Daily
COD (soluble & tota	2/Day	-	Daily
NO3-N	4/Wk	-	4/Wk
NH3-N	4/Wk	-	4/Wk
TKN	4/Wk	-	4/Wk
DPA	3/Wk	3/Wk (sludge)	3/Wk
2-N-DPA	3/Wk	3/Wk (sludge)	3/Wk
DBP	3/Wk	3/Wk (sludge)	3/Wk
NG	3/Wk	3/Wk (sludge)	3/Wk
MLSS	Daily	-	Daily
MLVSS	-	Daily	-

5.5 Process Characterization

5.5.1 EA Mass Transfer Studies

Volatilization of EA: In order to quantify the volatilization of EA during aeration cycles, stripping tests were conducted. For these experiments, the top of the reactor was completely sealed and off-gases were diverted through a small vent. An organic vapor adsorption assembly (SIPEN: Model SP1) consisting of a vacuum pump and two activated carbon columns placed in series sampled off-gases at a rate of 0.1 L/min. The columns were replaced periodically to ensure that they were not exhausted. The vapor trap was turned off at the end of the aerobic cycle (8 hrs) and columns stored at 4 °C for further analysis. EA accumulated over the eight hour period of aeration was analyzed using carbon disulfide extraction and gas chromatography (NIOSH analytical method S49). Subsequent analyses confirmed that the series trap configuration was sufficient to adsorb EA without breakthrough.

5.5.2 Temporal Profiles

Concentration-time profiles of various constituents were quantified to gain insight into the fate of various compounds. Temporal profiles also provide quantitative information on the lengths of aerobic and anoxic react phases needed to be adopted to achieve the desired degree of conversion. For these experiments, samples from the reactor were collected at periodic intervals within each cycle, and immediately filtered through a 0.45μm membrane to stop further biodegradation. Analysis for aqueous phase concentrations of COD and NG was performed immediately while analysis of NO_3-N, conducted only for the samples collected during anoxic phase, was done 12 hours later. Once the concentration of NG in aqueous phase dropped below detection limit sludge samples were analyzed for NG for the remaining cycle time in order to quantify the removal of NG due to biosorption. For these experiments, 250 ml of mixed liquor samples were

collected at periodic intervals and immediately filtered through 0.45 mm membrane and stored at 0 °C. The biomass retained on the membrane was analyzed for NG 12 hours later. Measurement of biomass retained on the membranes on a dry weight basis provided the mixed liquor concentration at each sampling point. A sludge sample taken prior to initiation of fill was also analyzed to obtain background concentration of NG.

5.6 Bench Scale Study

Although amenability of NG to biodegradation is documented in the literature [34, 29], it remains unclear whether NG can serve as a sole carbon source supporting microbial growth. Wendt *et al.* [21] reported NG to be an unsuitable carbon source when supplied as a sole source of carbon to bacteria. The conclusion that NG is an unsuitable carbon source reported in this study [21] was based on evidence that a mixed culture of organisms was unable to degrade NG in absence of glucose. Reasons for failure of an inoculum to bring about biodegradation are numerous, the most likely being insufficient population of degrading species, unsuitable environmental conditions (aerobic or anoxic), unacclimated cultures, substrate toxicity and/or recalcitrance. Consequently, laboratory-scale batch culture experiments and BOD assays were conducted to investigate the potential of NG to serve as a sole carbon source. The batch culture experiments were designed to eliminate the first three possible causes for the failure of the inoculum to facilitate biodegradation. For these studies, two sets of experiments with similar feed composition, were conducted in 5 L batch reactors, separately under aerobic and anaerobic conditions each with an average F:M ratio of 0.08. To avoid substrate toxicity the F:M ratio for bench scale studies is lower than the pilot scale study. The feed contained 200 mg/L of NG, the only carbon source, dissolved in a nutrient broth similar to that used for BOD assays to provide all the essential nutrients. Since NG is available in a mixture containing 50% EA by weight, pure NG was obtained by evaporating EA until the weight dropped to half of its initial value. To

ensure that the nutrient broth is not deficient in the trace inorganic nutrients, 100 ml of tap water for every 1000 ml of feed was added. Since 200 mg/L of NG exerted approximately 100 mg/L of COD, 5 mg/L of NH_3-N and 1 mg/L of phosphorous were added in addition to these nutrients already present in the nutrient broth. The reactor was seeded with NG-acclimated biomass obtained from the pilot scale reactor. MLVSS of the batch reactors was measured to be approximately 3000 mg/L. The aerobic reactor system was aerated with filtered and humidified air (D.O. $\geq$ 5 mg/L) and agitated with a magnetic stirrer. The anoxic reactor system was sealed and the culture was agitated with a magnetic stirrer. For both experiments, biomass was allowed to settle at the end the of react phase and the supernatant analyzed for NG.

BOD assays were conducted to study the potential of NG to serve as a sole carbon source under low substrate concentrations. Assays were conducted with three types of substrates: NG alone at 200 mg/l (three replicates at various dilutions), EA alone at 450 mg/l (eight replicates), NG and EA together at 200 mg/l and 450 mg/l (eight replicates), respectively. The bottles were seeded with effluent from the pilot plant treating NG ladened wastewater.

6. Results and Discussion

6.1 Process Performance

As a result of a seven day lag on the priority pollutants and NG results from the commercial laboratory and a five day lag on BOD results, daily process performance was estimated based on effluent COD (total) (Fig 6.1) and total suspended solids (TSS) results (Fig.6.2). A correlation developed between effluent COD and BOD results obtained from phase I was used as criteria to calculate effluent BOD based on daily effluent COD data. Subsequent effluent BOD results showed no significant deviations from the correlated values. Fig. 6.3 illustrates the impact of NG on the degradation of other organic compounds during acclimation and process performance evaluation periods based on daily effluent BOD results. The average effluent BOD (total) for the first half of phase II was 26 (± 12.82) mg/l. The average effluent BOD (total) for second half of phase II was 13 (± 2.92) mg/l and for phase III was 7.18 (± 7.13) mg/l. The effluent total suspended solids were consistently below permissible limits throughout the study (Fig. 6.2). The average effluent TSS for the first half of phase II was 19 (± 8.35) mg/l. The average effluent TSS for second half of phase II was 15 (± 3.3) mg/l and for phase III was 21 (± 7.6) mg/l. The average effluent COD (total) for the first half of phase II was 65.7 (± 11) mg/l. The average effluent COD (total) for second half of phase II was 42 (± 7.3) mg/l and for phase III was 53 (± 10) mg/l. The results of effluent COD, BOD, and TSS although consistently below the permissible limits, exhibited considerable fluctuations during phase I and early half of phase II. However, the average values and the amplitude of fluctuations decreased considerably during the later half of phase II and phase III. The improved efficiency of system performance may be a result of longer static-fill period adopted during SBR cycle scheme B.

Fig 6.1: Influent and Effluent Total COD

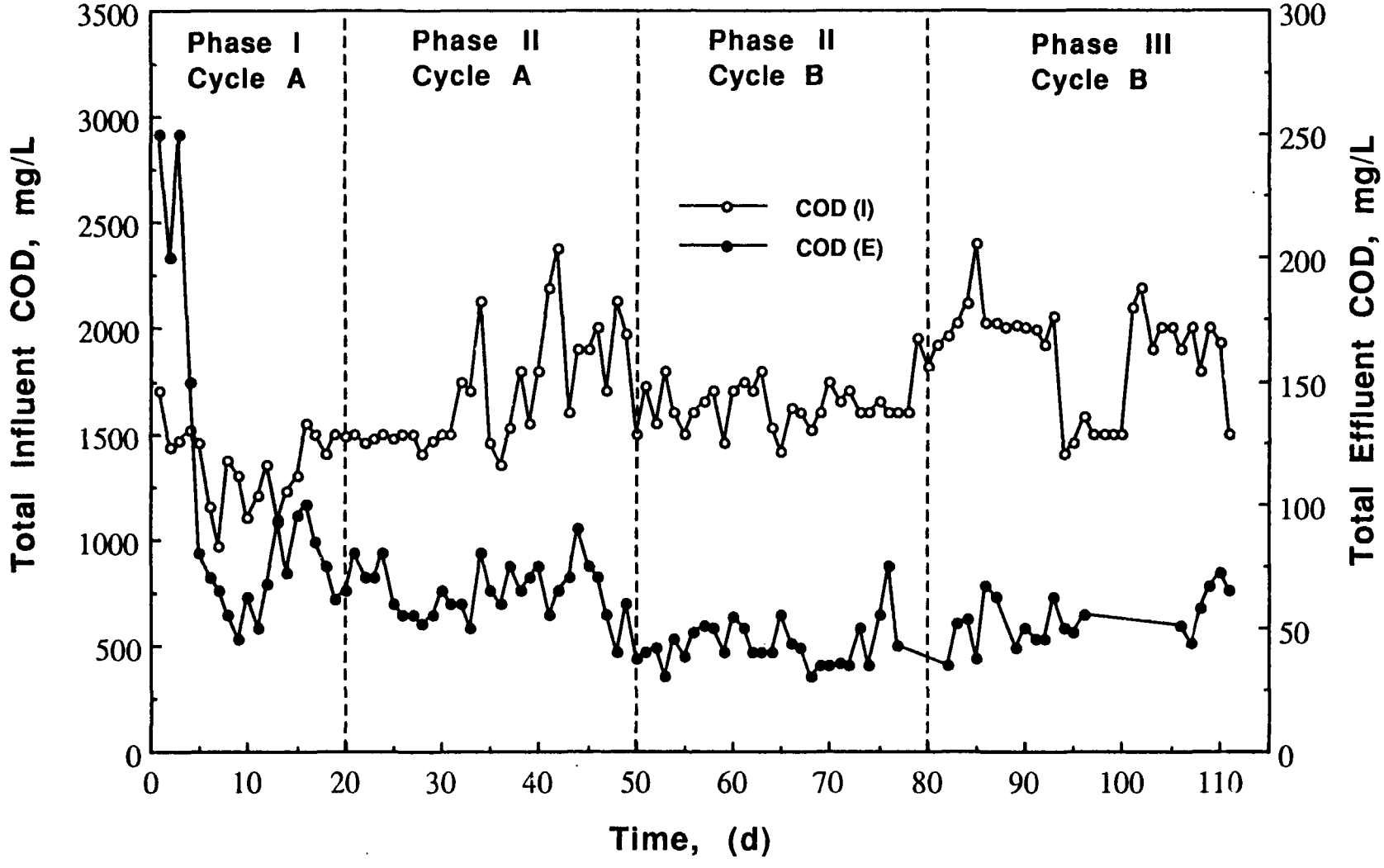


Fig 6.2: Effluent Total Suspended Solids

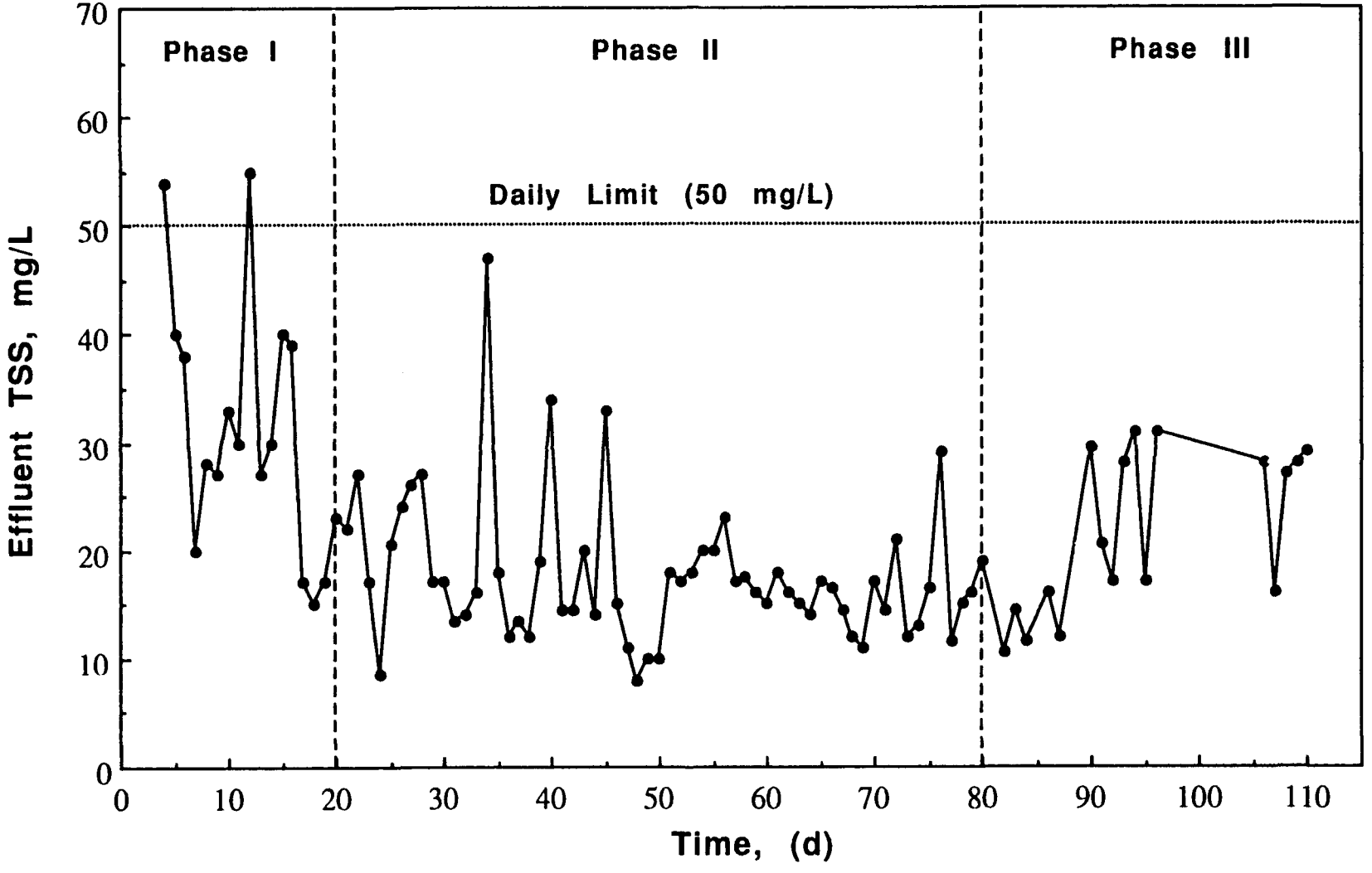


Fig 6.3: Influent and Effluent Total BOD

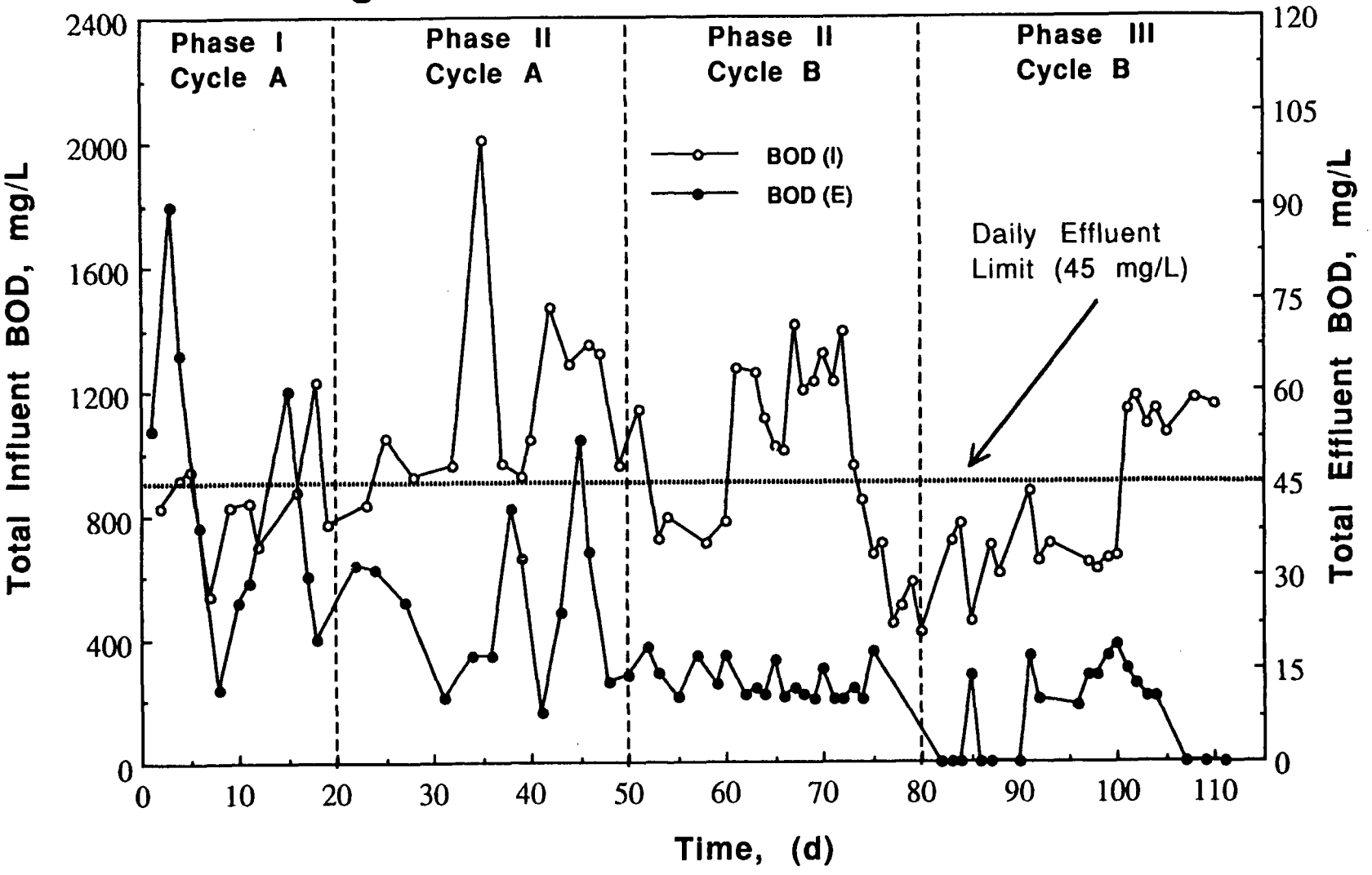


Fig. 6.4: Influent and Effluent DBP

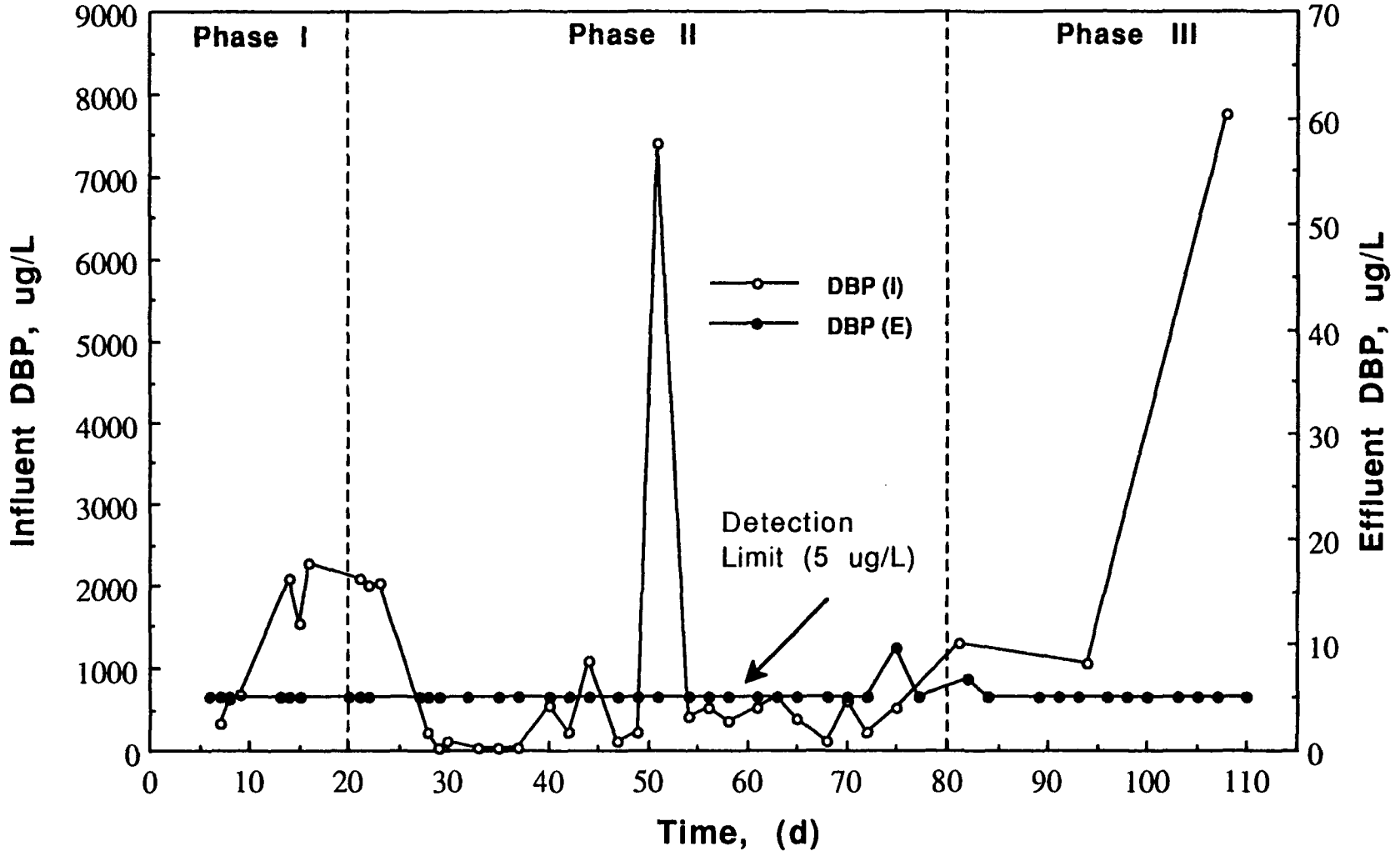


Fig. 6.5: Influent and Effluent DPA

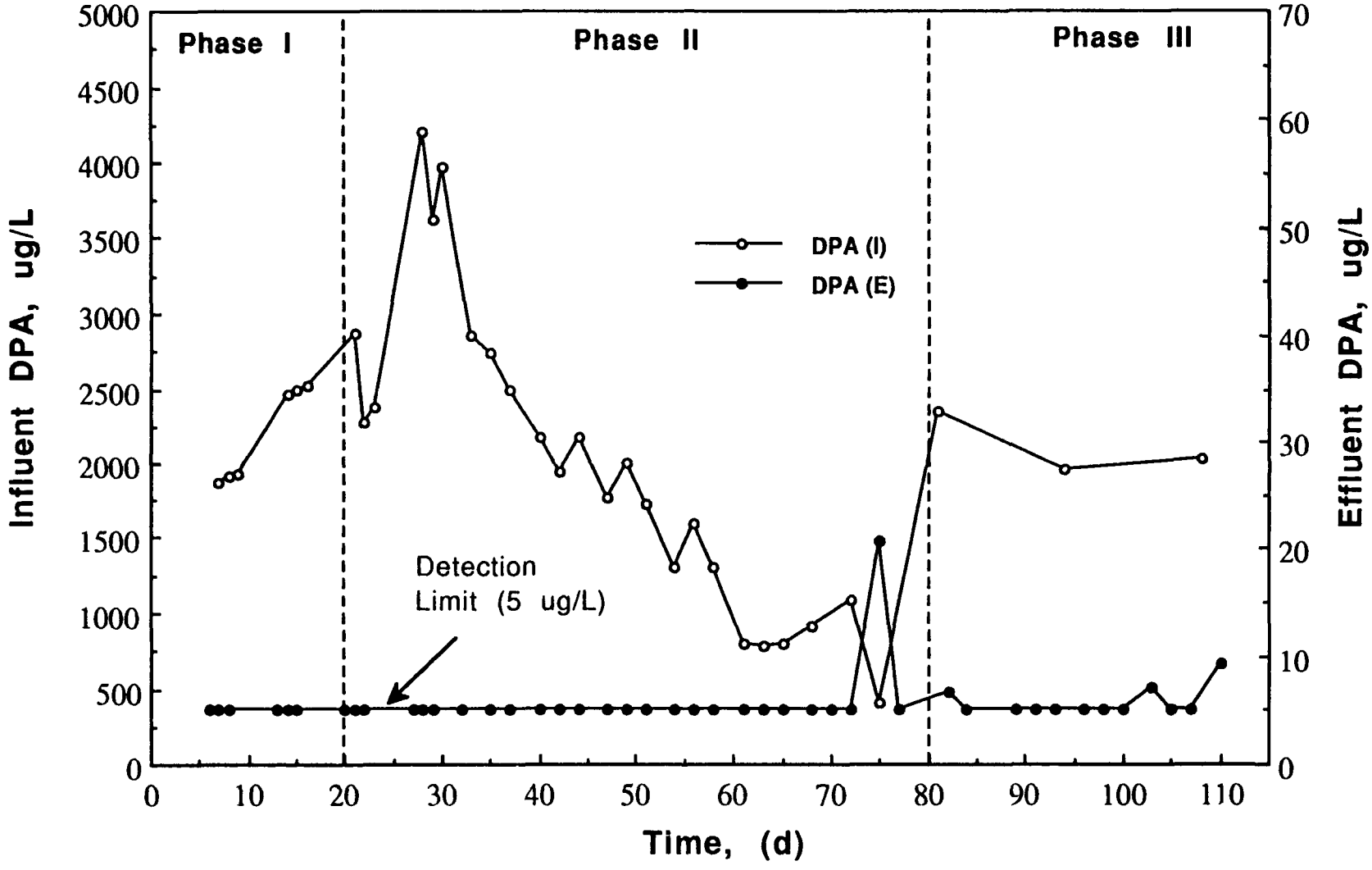


Fig. 6.6: Influent and Effluent 2-N-DPA

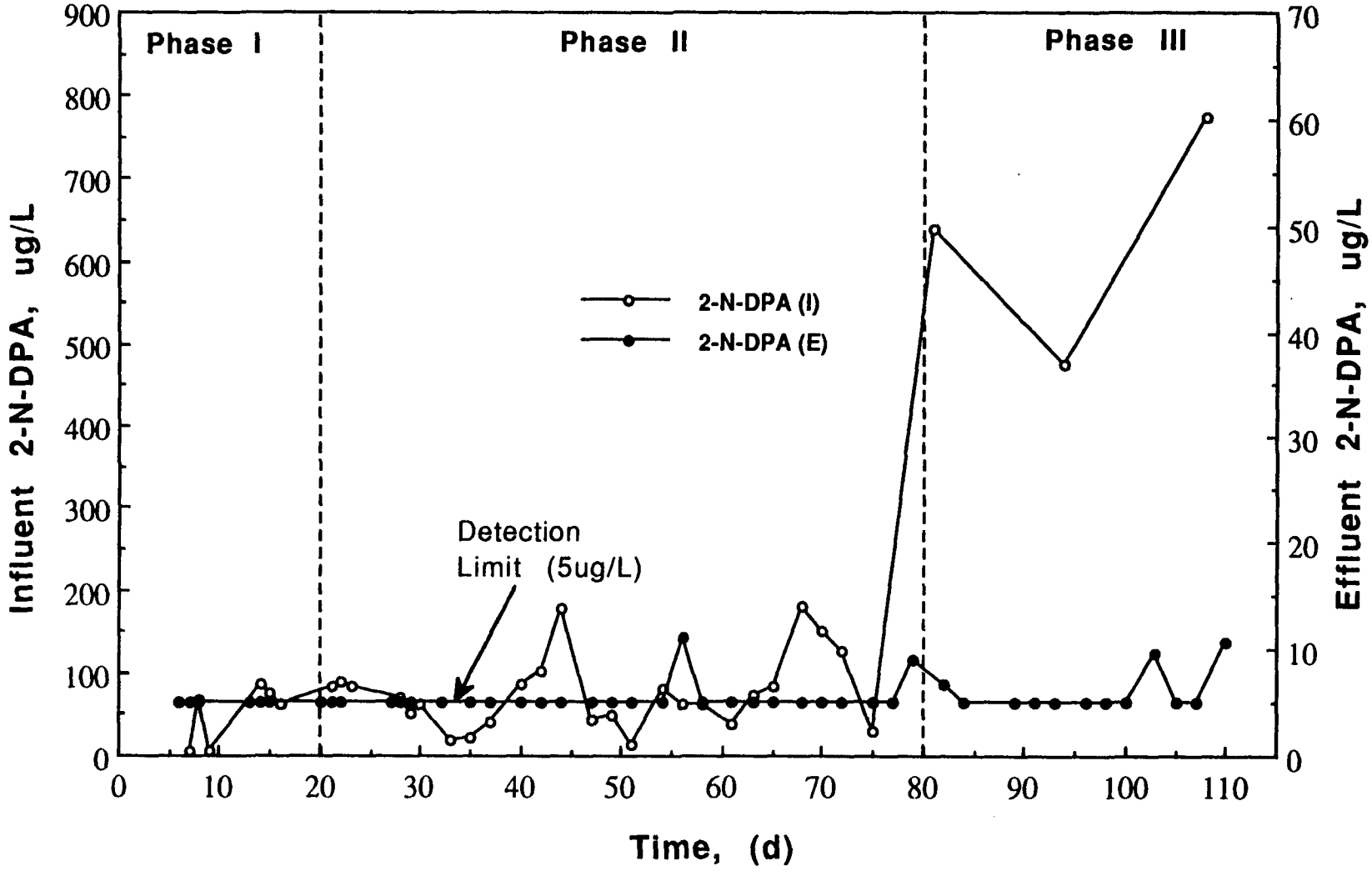
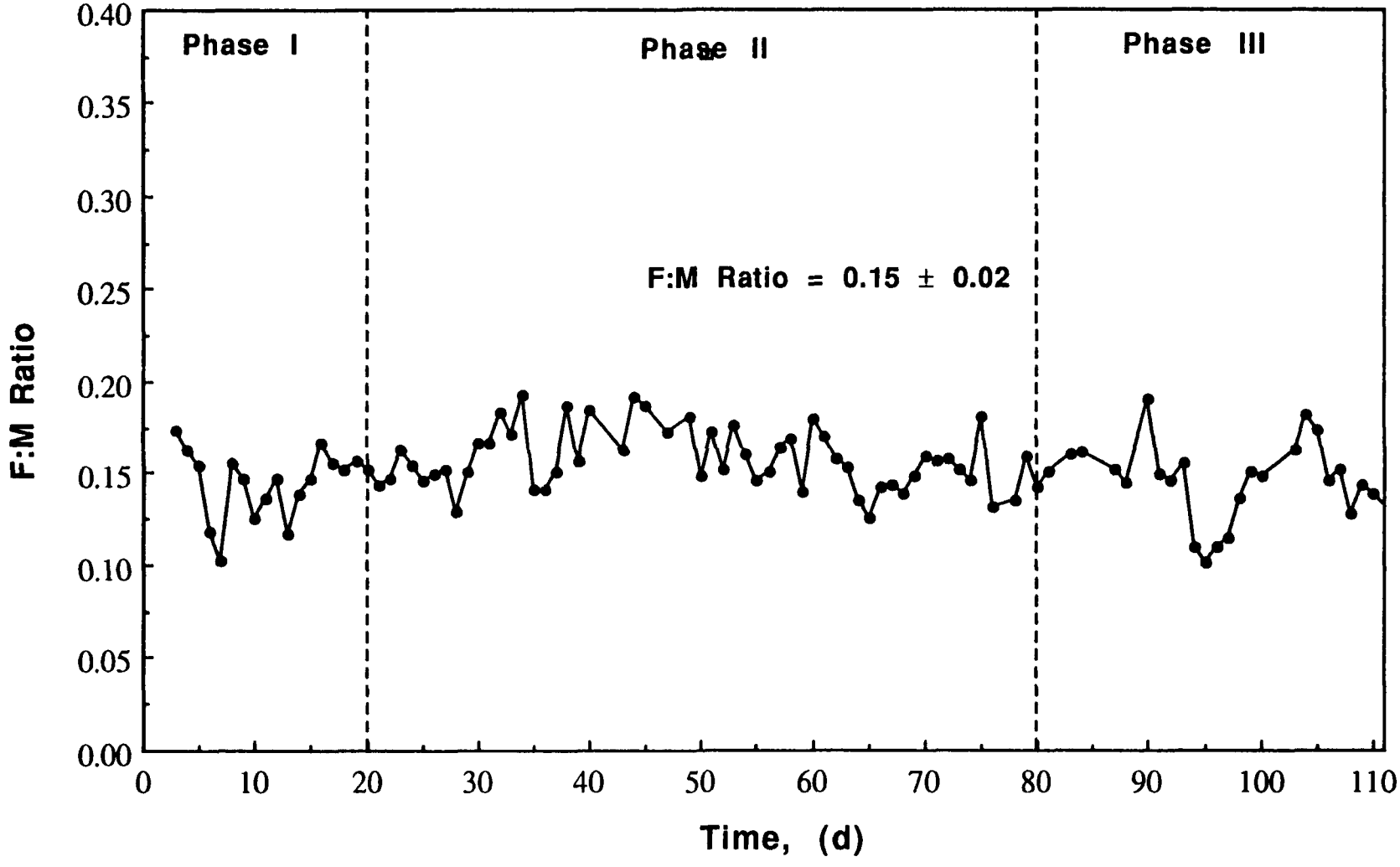
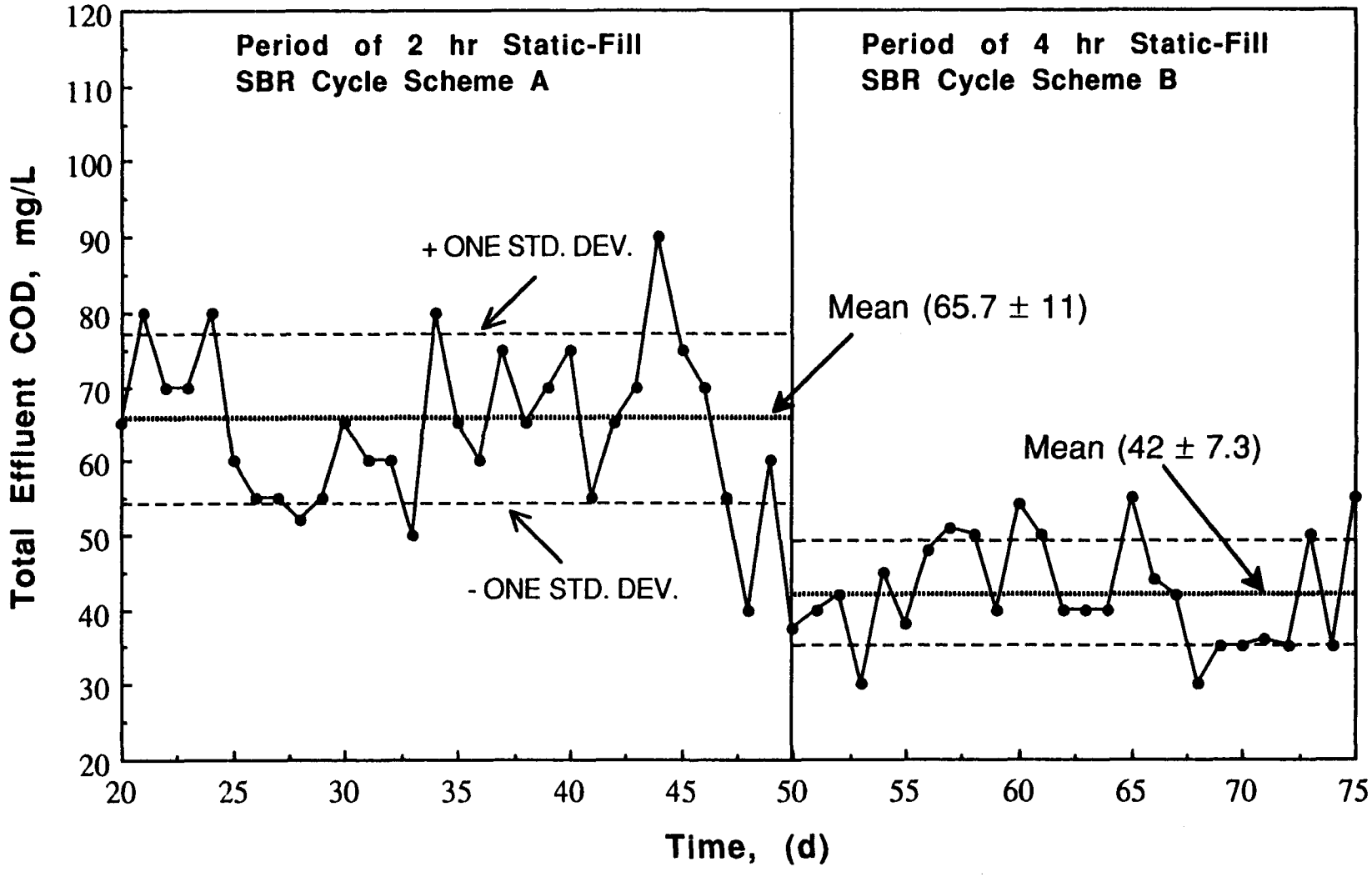


Fig. 6.7: Daily F:M Ratio



At concentrations investigated, NG was found not to exhibit toxic behavior or adversely impact the removal of priority pollutants.Figs. 6.4, 6.5, and 6.6 illustrate the influent and effluent concentrations of priority pollutants, DBP, DPA, and 2-N-DPA, respectively. Although influent concentrations of priority pollutants were inconsistent, effluent concentrations were regularly below permissible limits (5 μg/L). These results clearly indicate that the addition of NG did not adversely impact their removal. The dependence of removal of priority pollutants on the F:M (Fig 6.7) ratios as reported in the A.D. Little, Inc. study [1] was not observed in the present study. Priority pollutants are toxic in nature and hence their utilization does not occur until the more readily biodegradable substrates takes place. Since degradation of toxic compounds occurs during the endogenous growth phase, provision of long aerobic phase may have obviated the dependence of F:M ratios on the removal of priority pollutants. Although some amount of biosorption was noticed, a mass balance on priority pollutants showed that their removal was primarily due to biodegradation. In essence, NG was found not to be toxic and exhibited no adverse impact either on the removal of priority pollutants or on meeting effluent standards within the operating concentrations.

Fig. 6.8: Total Effluent COD for SBR Cycles A and B



6.2 Impact of Static-Fill Time

SBR cycle scheme A (Table 5.1) was adopted for three weeks of phase I and the first four weeks of phase II. For this period the average effluent COD (total) was 65.7 mg/l (33 points) with a standard deviation of 11 mg/l. The last four weeks of phase II and five weeks of phase III were operated with the SBR cycle scheme B (Table 5.1) in an attempt to study the impact of longer fill and shorter idle phases. With this scheme the average effluent COD (total) was 42 mg/l (27 points) with a standard deviation of 7.3. A t-test performed on this data at a 5% rejection level showed a statistically significant difference in the mean value of effluent COD (total) for two schemes. A comparison of results of these two schemes clearly indicates a significant improvement in the quality of effluent with the later SBR cycle scheme. Fig. 6.17 shows the comparison of total effluent COD for both scheme A and scheme B of SBR cycle. Not only was there a statistical improvement with the later SBR cycle scheme, but there also was a dramatic visual improvement in the quality of effluent.

6.3 Mechanism of NG Degradation

The results of influent and effluent NG concentrations of the pilot scale study both during acclimation and during system performance evaluation phases are illustrated in Figure 6.8. The results clearly demonstrate that NG is biodegradable and can be removed to below detection limits using acclimated sludge. Although total removal of NG was observed, it was unclear during which cycle, either aerobic or anoxic conditions, the degradation was occurring, since both the conditions were present in the SBR schemes. To ascertain the environmental conditions under which degradation of NG is taking place, NG concentration-time studies were conducted. Results on reactor NG temporal concentrations (Fig. 6.9) show that the NG aqueous concentrations dropped below detection limits (5 mg/l) within five hours into the aerobic phase. But, NG is a

Fig. 6.9: Influent and Effluent NG

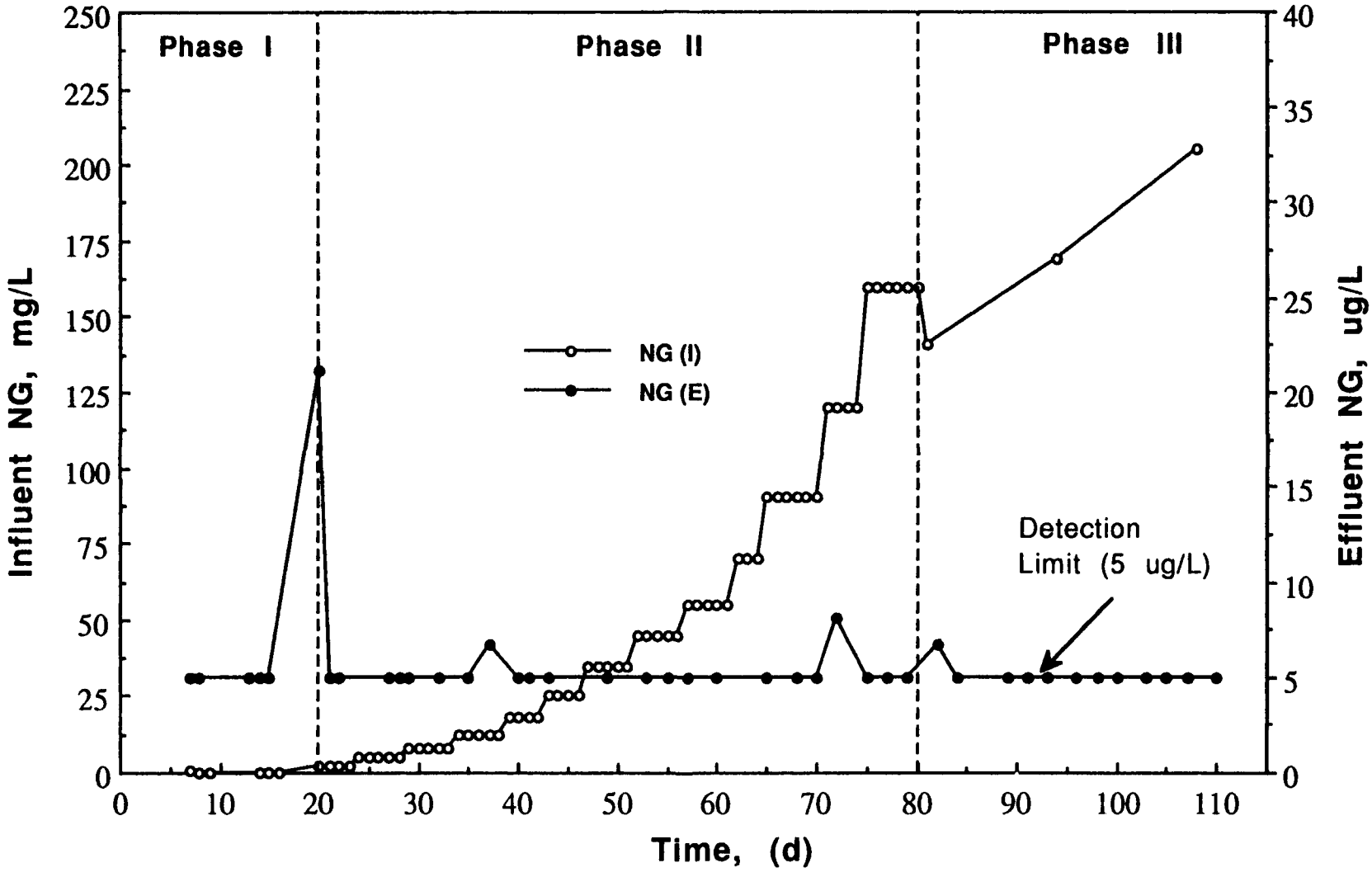


Fig. 6.9: Reactor NG temporal profile

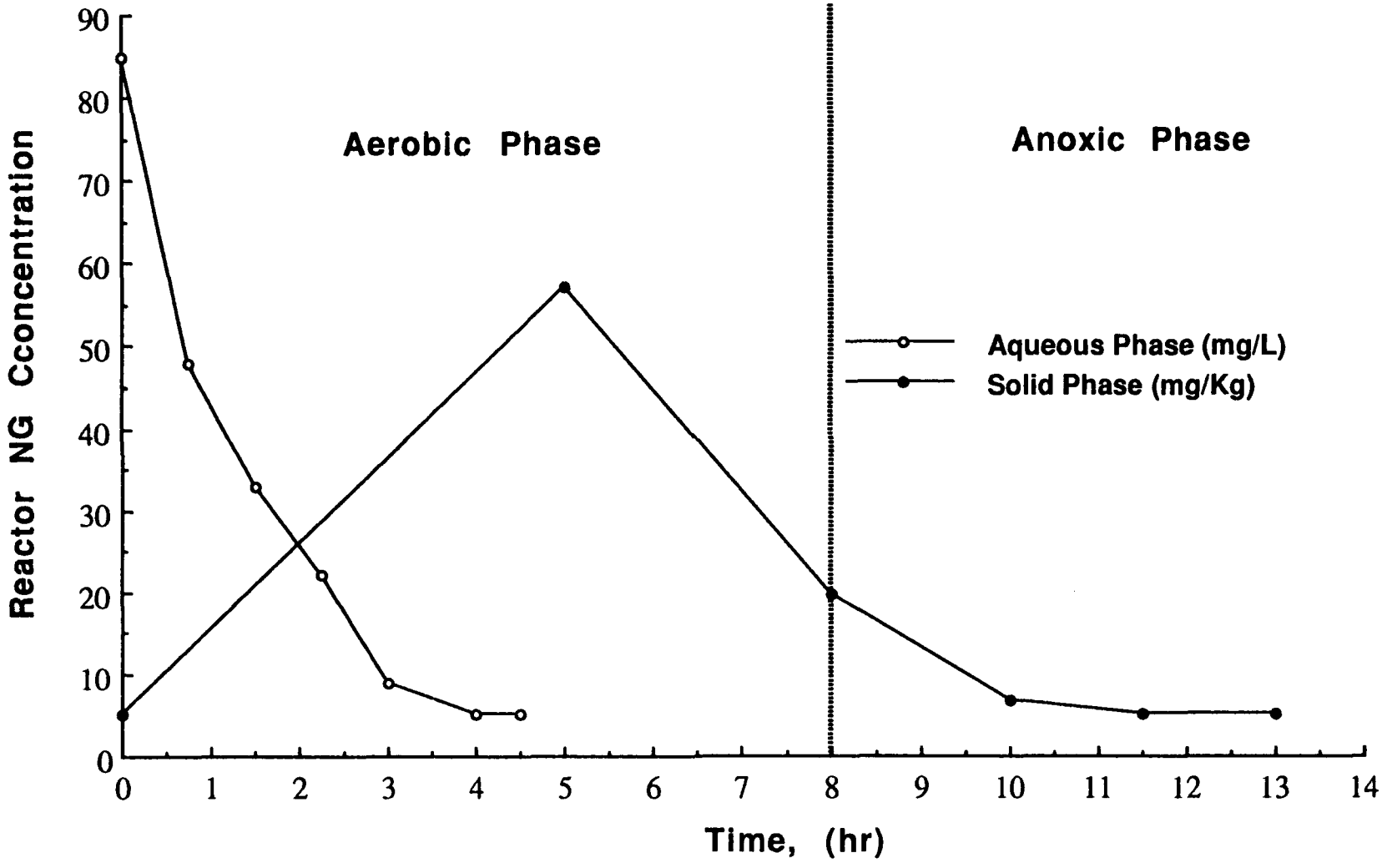
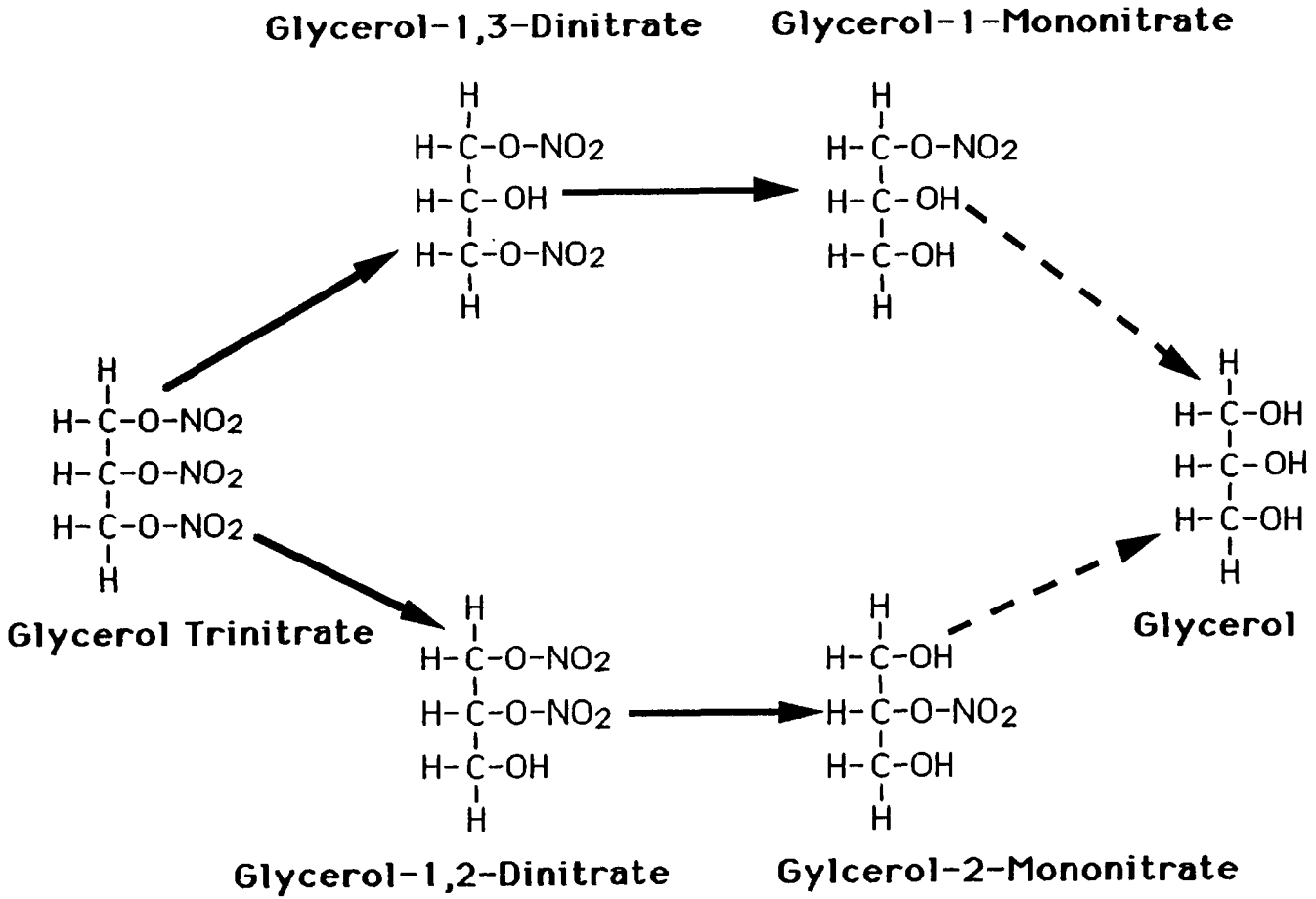


Fig 6.11 NG Degradation Pathway*



*Adapted From Wendt et al.

hydrophobic substance with moderately low solubility (1.8 mg/L at 20 °C [32]), therefore the possibility of its removal by a non-biological mechanism, biosorption, was also explored (Fig.6.9). Once the aqueous phase concentration was below detection limits, the mass of total solid (sludge) phase NG was measured to be 115 mg. Comparing this value to mass of NG (aqueous phase) present in the reactor at the initiation of the react cycle (3200 mg), indicates that 96.4% of it was degraded within the first five hours of aeration with no appreciable (< 4%) accumulation in the biofloc. The amount of biosorption is in agreement with the observations of earlier studies [34]. Since NG exerts a low vapor pressure (0.00026 torr at 20 °C [32]), its removal due to volatilization is more likely to be negligible. From Fig. 6.9, it is also interesting to note removal of biosorbed NG occurred even under anoxic conditions. Given the fact that the DO concentration in the reactor dropped below 1 mg/L after 15 minutes into the anoxic phase, it appears that NG is amenable to anoxic, as well as aerobic degradation. The results of the pilot scale study (Fig.6.8) adequately demonstrate that NG is biodegradable aerobically. Moreover, given that majority of NG is removed during the early part of aerobic cycle, its removal took place when the biomass is actively metabolizing the growth substrates but not during the secondary growth phase.

A possible metabolic pathway in the degradation of NG given by Wendt *et al.* [34] is illustrated in Figure 6.10. The breakdown of NG, from this pathway, is believed to take place stepwise via dinitrate and mononitrate esters. The carbon skeleton of the molecule of NG is glycerol, which is metabolized by many bacteria and fungi under aerobic and microaerobic conditions. The sequence of physiological events that occur during glycerol catabolism include facilitated diffusion into cells through a specific glycerol permease, phosphorylation by a glycerol kinase, and oxidation by a membrane bound glycerol-P-dehydrogenase to glyceraldehyde-3-P. The latter enters the triose-phosphate portion of

glycolysis. Since one adenosine triphosphate (ATP) is expended, and reducing power is generated to make glyceraldehyde-3-P, the redox balance and energy yield is such that glycerol cannot be fermented. Nevertheless, nitro groups of NG may provide reducible sites for microbial consortium members to use for re-establishing an appropriate redox balance during anaerobic growth, possibly explaining the degradation of NG during anoxic conditions.

6.4 Bench-Scale NG Results

Bench-scale studies were conducted to determine the capability of NG to independently support biological growth. Fig 6.11 shows the results of the bench-scale batch reactors when NG was provided as the sole carbon source. Using acclimated biomass, a 6% reduction under aerobic and no measurable reduction under anoxic conditions in the effluent NG concentrations was observed. This finding is in agreement with the previous work [34] that reported a 3.1% decrease in NG concentration in shake-flask experiments in the absence of growth substrate. To further investigate the issue of NG as a growth substrate, BOD assays were conducted using NG and EA, singly and in combination. Fig 6.12 summarizes the results of BOD assays. The results showed no change in D.O. concentration when NG alone was used as substrate. Application of Student-t test indicates that there is no statistical difference at 95% significance level between the BOD exerted by the EA alone sample and EA and NG sample. These findings support the hypothesis that NG cannot be utilized as a sole carbon source either in aerobic or anoxic environments. However, aerobic degradation of NG in the presence of growth supporting substrates in the pilot-scale study suggests that it may have behaved as a non-growth substrate. The recent findings on the biochemical significance of co-metabolism reveal that the accidental utilization of non-specific enzymes

Fig 6.12: Bench Scale Biodegradation Study

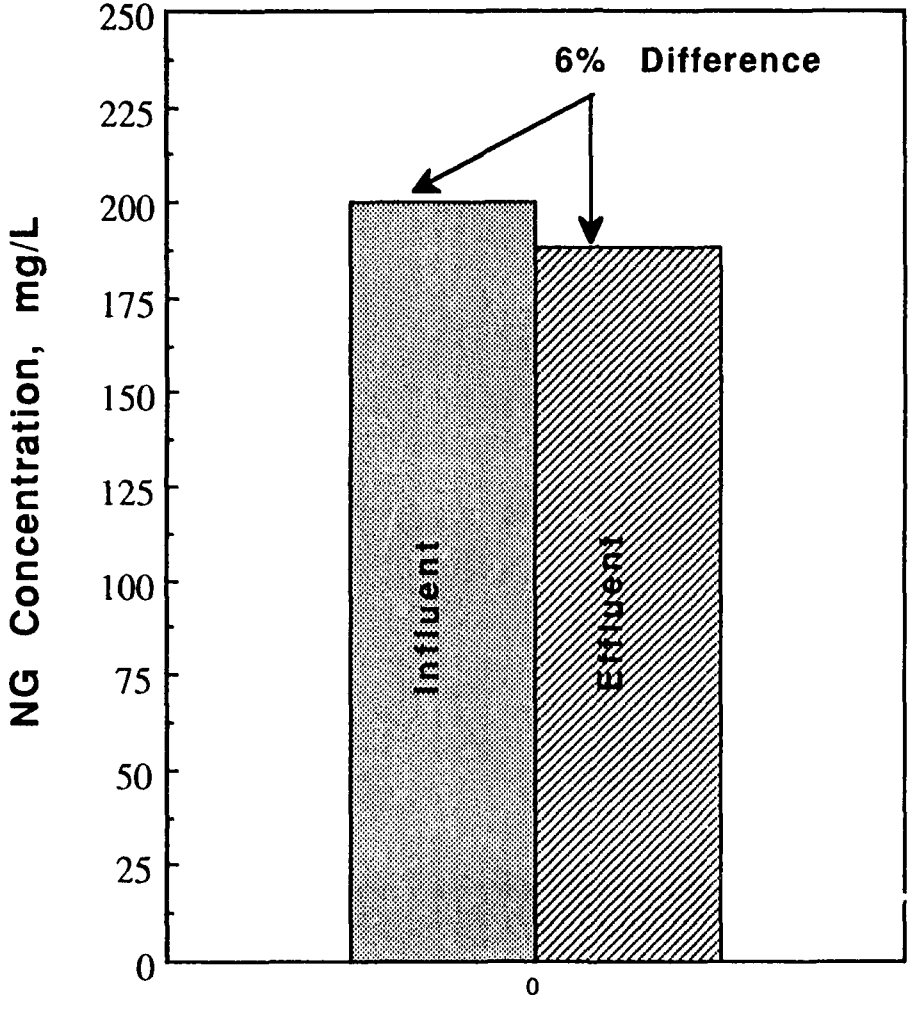
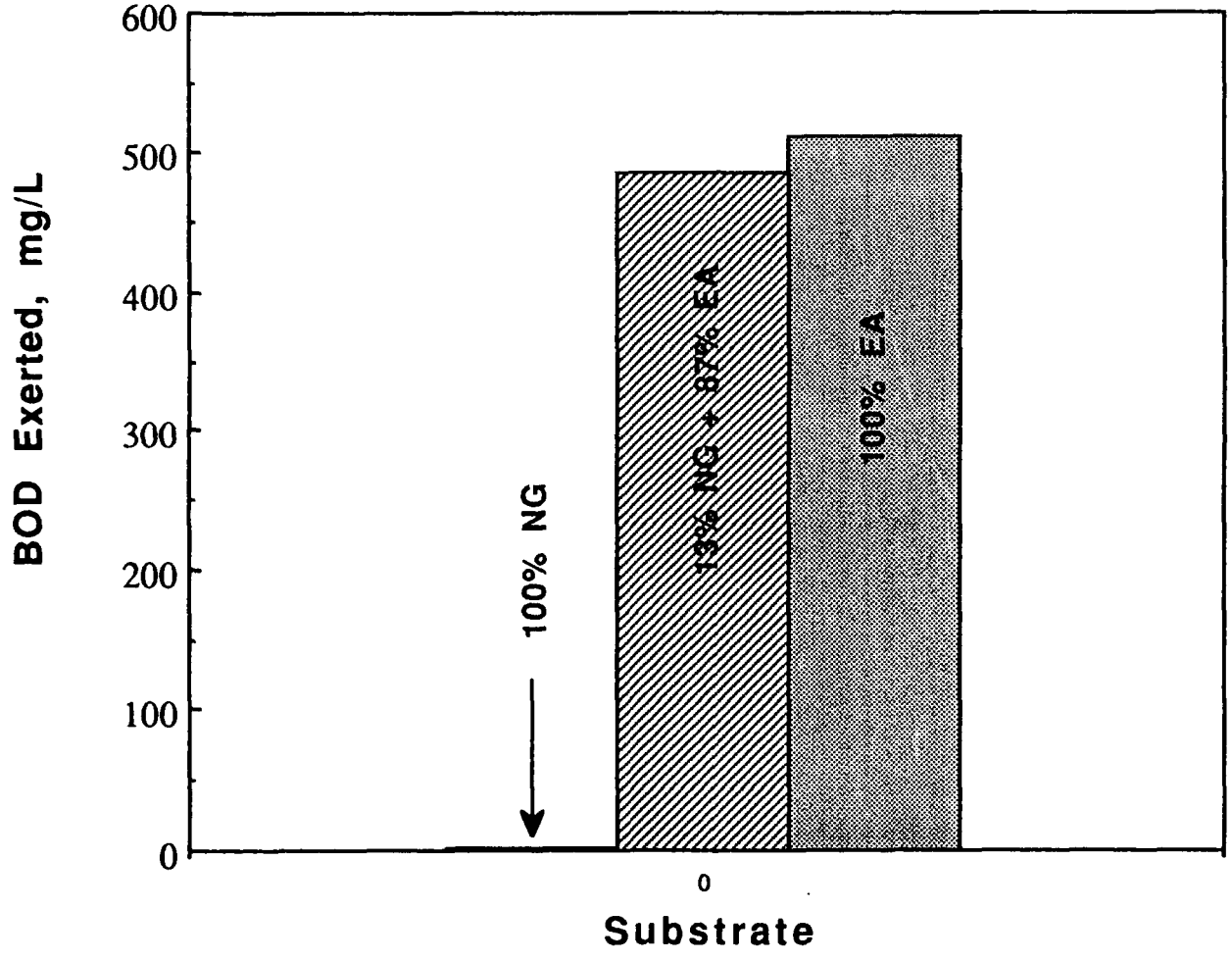
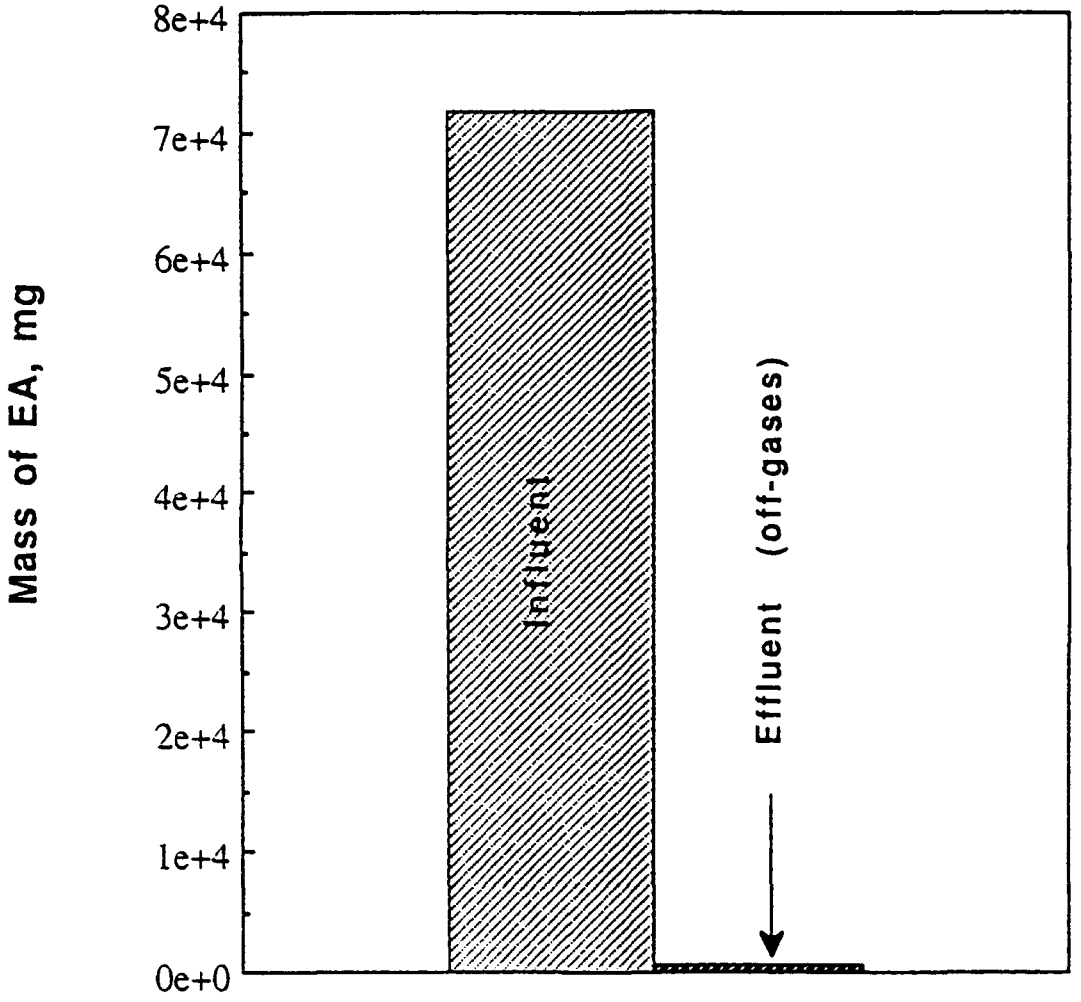


Fig 6.13: BOD Assays for Various Substrates



induced by the growth substrate to be directly responsible for the transformation of non-growth substrates [22]. As a result, complete transformation capacity is realized only when sufficient suitable growth substrate is present to mobilize the required quantities of enzymes. The deterioration of NG removal efficiency observed in the RAAP study [29] when COD to NG ratio was lowered and the dependence of NG metabolism on endogenous glutathione reserves [20] demonstrate the need for sufficient growth substrate for NG transformation. Based on these reports, and our results, it appears that degradation of NG occurs aerobically through co-metabolism. Although more definitive testing is required to validate this hypothesis, the consequences of these findings could be of major significance. It is clear that if stable system performance is to be realized sufficient growth substrate must be available in the influent to ensure co-metabolism of NG. This may require the addition of external suitable carbon source to supplement the influent BOD, especially if the NG concentrations become excessive.

Fig 6.14: Volatilization of Ethyl Acetate



6.5 Volatilization of the Growth Substrate:

Air-stripping has been considered to be a primary mechanism for removal of volatile organic compounds (VOCs) during aerobic biological treatment of wastewaters. Further, volatilization of VOCs may significantly reduce the amount substrate available for biomass growth, adversely impacting the performance of biological treatment systems. Volatilization of growth substrates can have profound effects if degradation of ancillary compounds occurs via co-metabolism. Loss of volatile growth substrate due to aeration may reduce the stoichiometrically available amount of carbon source for co-metabolism, resulting in a poor system performance.

The growth substrate, EA, has a gas/liquid partitioning coefficient of approximately 10^{-4} atm-m^3/mol @ 20 °C [32], indicating a semi-volatile nature. Volatility of the growth substrate is of primary concern if degradation of the targeted compound occurs through co-metabolism. Volatilization of EA was quantified through mass balance calculations. Since the rates of air supply to the SBR and sampling off-gas were known, an EA mass balance could be performed. The amount of EA adsorbed on the carbon columns for the period of aeration was determined analytically. Knowing the amount of EA adsorbed on the carbon columns and the fraction of air sampled, the total amount of EA that volatilized from the reactor during aeration was calculated.

A comparison of amounts of EA present in the reactor prior to aeration and in off-gases during aeration revealed that losses due to volatilization, over eight hours of aeration, averaged less than 1% of total EA initially present. In similar studies, Kincannon et al. [18] reported a 7% volatilization of EA from laboratory-scale activated sludge reactors. EA appears to be suitable growth substrate for NG degradation both in terms physicochemical as well as biochemical properties.

6.6 Nitrification/Denitrification

6.6.1 Nitrification

When a microbial consortia is exposed to a multicomponent waste stream, the various species of bacteria present at steady state in the mixed culture is dictated by the composition of the waste. When heterogeneous bacterial culture is subjected to organic carbon, inorganic and organic nitrogen, heterotrophic bacteria utilizes exogenous carbon compounds for energy and growth while autotrophic bacteria obtains its energy from inorganic oxidations, utilizing carbon dioxide as source of carbon. The process of conversion of ammonia-nitrogen NH3-N to nitrate-nitrogen NO_3-N is called nitrification. The major nitrifying bacteria are of the genera *Nitrosomonas* and *Nitrobacter*. The conversion of NH_3-N to NO3-N is a two step process. *Nitrosomonas* oxidize NH_3-N to NO_2-N and *Nitrobacter* oxidizes NO_2-N to NO_3-N. Nitrosomonas can oxidize ammonia-nitrogen to nitrite-nitrogen, but cannot complete the oxidation of nitrite-nitrogen to nitrate-nitrogen. Likewise, Nitrobacter is limited to the conversion of nitrite-nitrogen to nitrate-nitrogen. Therefore, presence of both the communities of bacteria is required for the complete oxidation of ammonia-nitrogen. Since conversion of ammonia to nitrite is the rate limiting step in there complete oxidation of ammonia to nitrate, growth and reaction kinetics of nitrosomonas are taken for design considerations.

The theoretical stoichiometric equations for the growth of nitrosomonas and nitrobacter can be written as:

$$55\ NH_4^+\text{-}N + 76\ O_2 + 109\ HCO_3^- \xrightarrow{\text{nitrosomonas}} C_5H_7NO_2 + 54\ NO_2^- + 57\ H_2O + 104\ H_2CO_3 \quad (1)$$

$$400\ NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- + 195\ O2 \xrightarrow{\text{nitrobacter}} C_5H_7NO_2 + 3\ H_2O + 400\ NO_3^- \quad (2)$$

Or, for overall oxidation of ammonia to nitrate, from reactions (1) and (2),

$$NH_4^+ + 1.83\ O_2 + 1.98\ HCO_3^- \longrightarrow 0.021\ C_5H_7NO_2 + 1.04\ H_2O + 0.98\ NO_3^- + 1.88\ H_2CO_3 \qquad (3)$$

From equations (1) to (3) it can be concluded that approximately 8.64 mg of bicarbonate alkalinity HCO_3^- will be utilized per mg of NH4-N oxidized. Also, approximately 4.33 mg of O_2 per mg of NH4-N oxidized will be needed for the complete oxidation of ammonia to nitrate [14]. Since nitrification reduces bicarbonate alkalinity and increases the concentration of carbonic acid (H_2CO_3), the pH would tend to be reduced. Severe pH depressions can occur if the wastewater is not suitably buffered to account for the loss of alkalinity. The significance of pH depression in the process is that nitrification rates are rapidly reduced as the pH is reduced below the neutral pH of 7 [31] Therefore adequate alkalinity must be provided to ensure safe operation and to achieve required degree of conversion.

6.6.2 Denitrification

Nitrification is adopted to reduce the ammonia-nitrogen concentration before discharge so as to reduce oxygen demand associated with its oxidation to a receiving body of water. However, nitrification merely transforms the form of the available nitrogen but does not reduce the mass of the nitrogen discharged. Biological denitrification is frequently employed to reduce nitrate to nitrogen gas and discharge it to the atmosphere. Denitrification is a biological process of reducing nitrate to nitrogen gas by utilizing nitrate as the terminal electron acceptor for microbial respiration in the absence of molecular oxygen [14]. Most heterogeneous bacteria employed in the activated sludge systems are facultative in nature. Which means that the bacteria can survive both in the presence and absence of molecular oxygen. In absence of molecular oxygen, facultative bacteria utilize

nitrate as the terminal electron acceptor. There are two types of enzyme systems involved in the reduction of nitrate: assimilatory and dissimilatory. Assimilatory nitrate reduction converts nitrate to ammonia for use by the cell in the biosynthesis and functions when nitrate is the only form of nitrogen available. Dissimilatory nitrate reduction results in the formation of N_2 gas from nitrate, and is the one responsible for the denitrification of wastewater. Denitrification is a two step process in which the first step is the conversion of nitrate to nitrite. The second step carries the nitrite through two intermediates to nitrogen gas [14].

$$NO_3^- \dashrightarrow NO_2^- \dashrightarrow [\text{intermediates}] \dashrightarrow N_2 \qquad (4)$$

The perspective from which denitrification must be viewed is just the opposite of carbon oxidation process. In carbon oxidation systems, organic carbon serves as a electron donor and molecular oxygen acts as a electron acceptor. Therefore organic carbon must be the rate limiting component. The objective of denitrification is the removal of electron acceptor (nitrate) and hence sufficient amount of electron donor (organic carbon) must be available in order to make nitrate concentration rate limiting. In most combined treatment systems carrying out both the organic carbon oxidation and denitrification, the carbon source will be lacking during denitrification due to its utilization during carbon oxidation process which occurs early in the treatment train. Usually, a cheap carbon source such as methanol is externally furnished during denitrification to promote nitrate conversion to nitrogen gas [31]. However, it has been demonstrated that bacteria are capable of developing endogenous or extra cellular carbon reserves when grown under substrate rich conditions. These reserves can be later utilized for carbon and energy needs during substrate-deficient conditions such as denitrification [4, 27]. Operating the SBR with static-fill conditions, rich substrate conditions can be created which in turn may provide an

opportunity for the bacteria to generate endogenous resources. The endogenous denitrification capacity of the microorganisms was investigated in this study.

Theoretical stoichiometric relations of denitrification process show that bicarbonate is produced and carbonic acid is consumed when nitrate or nitrite is reduced to nitrogen gas. From the stoichiometry of denitrification, approximately 3.66 mg of bicarbonate alkalinity will be produced per mg of nitrate-nitrogen reduced to nitrogen gas. Therefore, tendency of denitrification is to partially reverse the effects of nitrification and raise the pH of biological reactions [31]. The use of oxygen as the final electron acceptor is more energetically favored than the use of nitrate. Therefore the greater free energy released for oxygen favors its use whenever it is available. Consequently, denitrification must be conducted in an anoxic environment to ensure that nitrate, rather than oxygen, serves as the final electron acceptor. As a general rule, if DO concentration in the aqueous phase is reduced to $\leq$ 1 mg/L, sufficient anoxic conditions can be created within the biological floc to eliminate the availability of molecular oxygen [14].

Fig. 6.15: Influent and Effluent Ammonia-Nitrogen

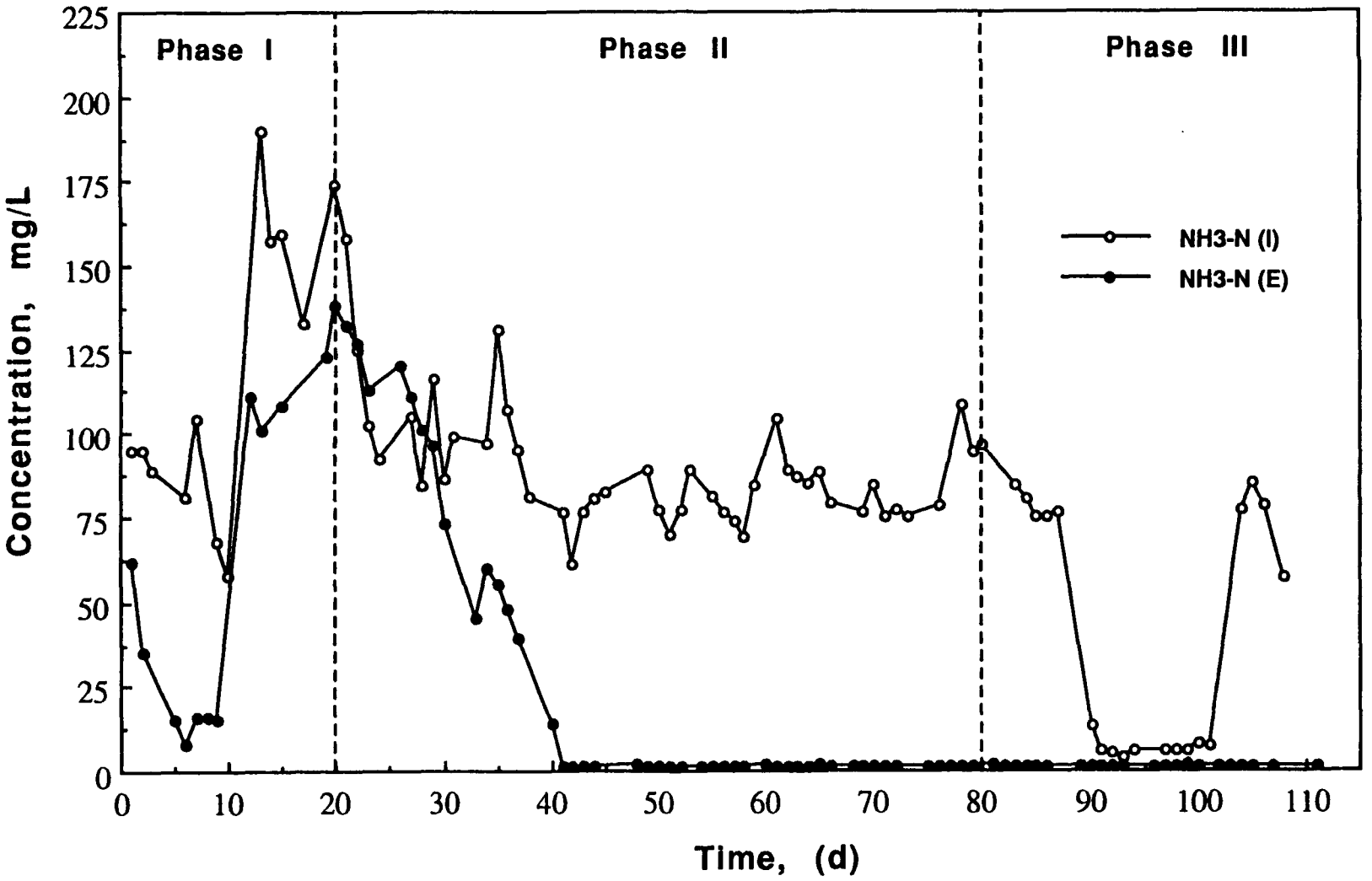


Fig. 6.16: Influent and Effluent Nitrate-Nitrogen

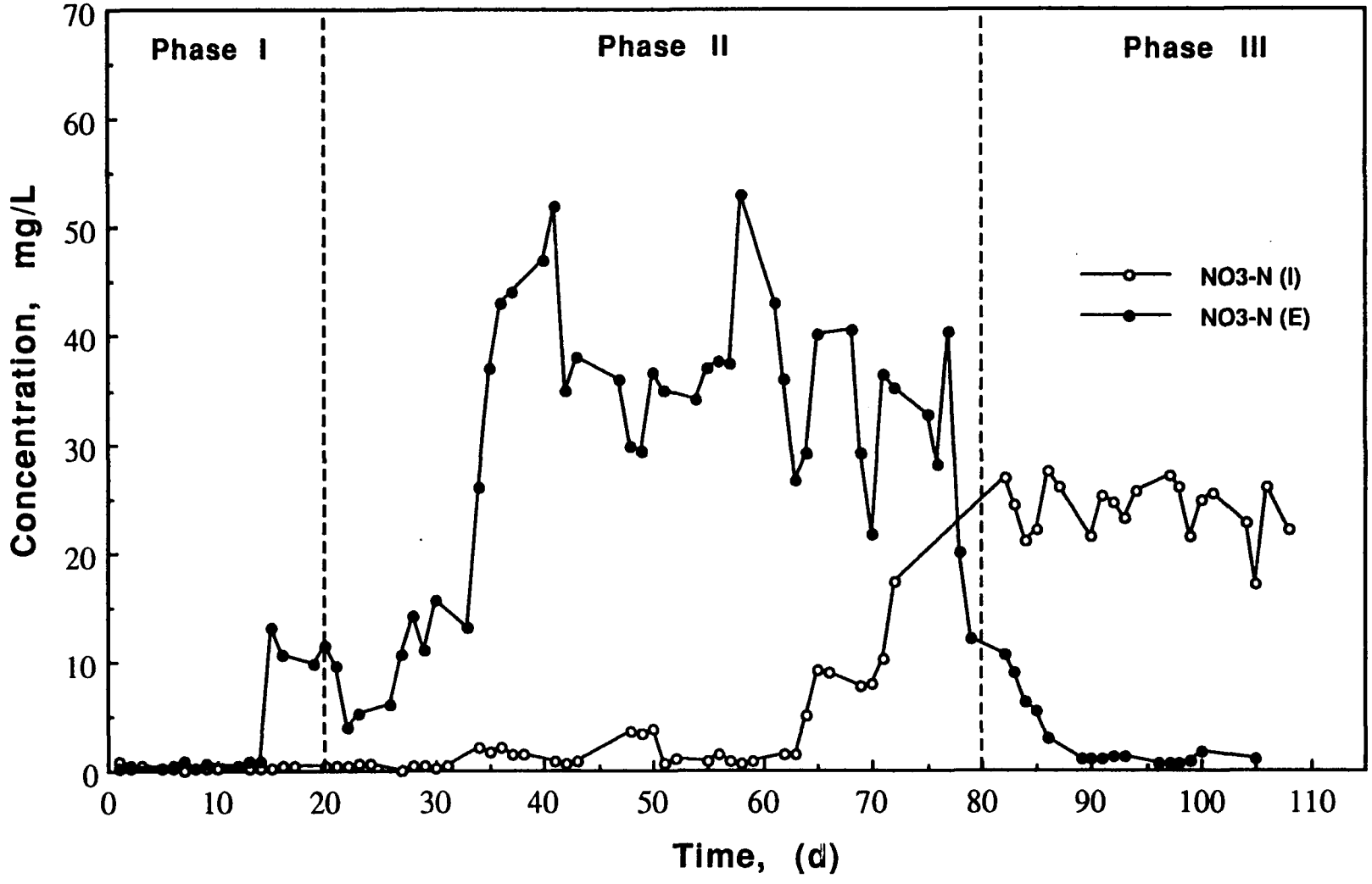
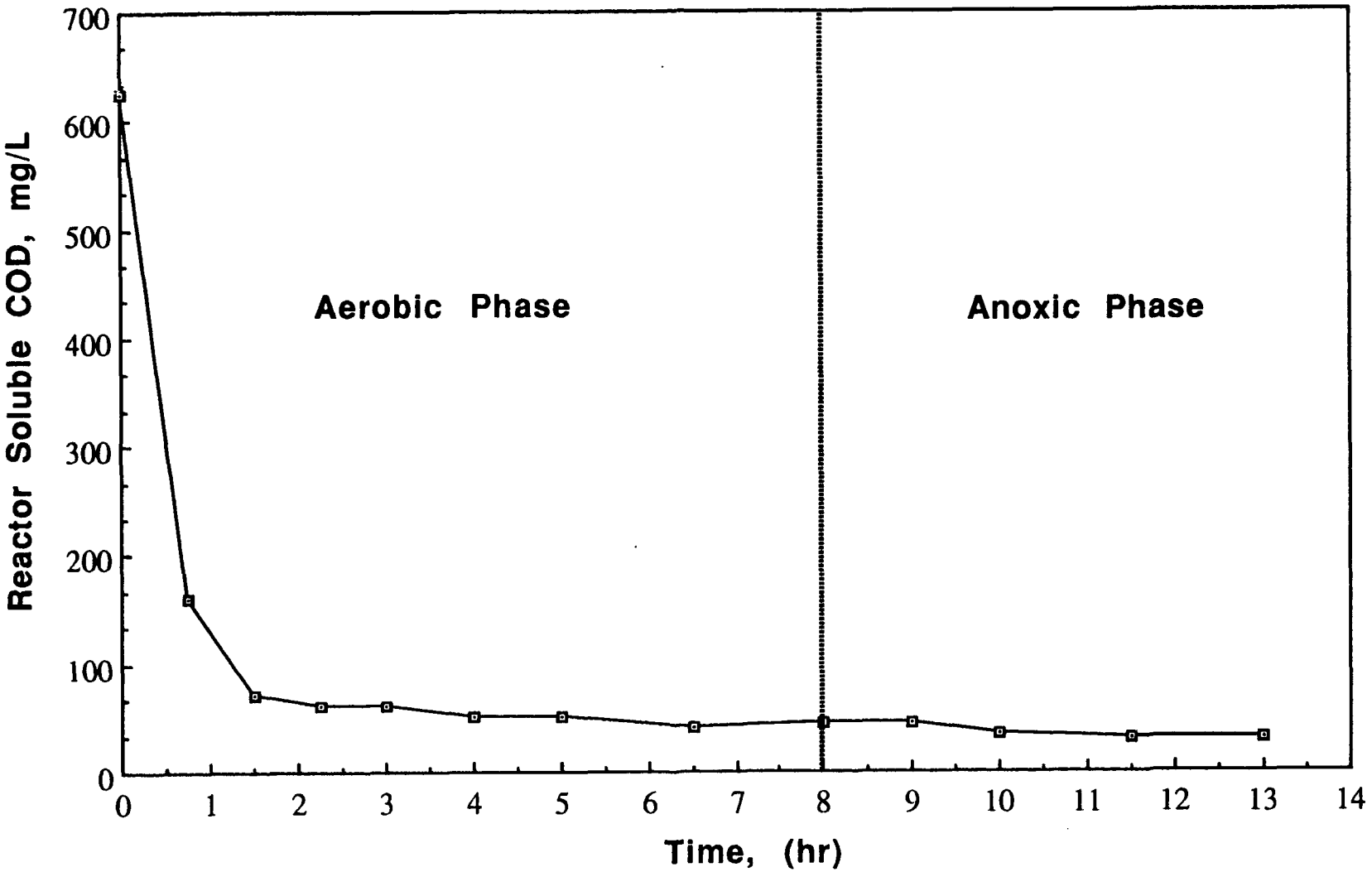


Figure 6.17: Reactor COD Temporal Profile



6.6.3 Nitrification and Denitrification Results

Figures 6.14 and 6.15, show the inventory of NH_3-N and NO_3-N, respectively. The results of TKN are illustrated in Appendix A-12. The high effluent NH_3-N concentrations (Fig. 6.14) demonstrated a decreasing trend from day 20 and dropped below detections limits after approximately 41 days. This type of trend generally observed during initial startups is typically due to lag phase in the growth of nitrifying bacteria. Nitrifying bacteria are slow growers and typically take 45 to 60 days to become established. Simultaneously, lag phase in the growth of nitrifying bacteria can be observed from effluent NO_3-N concentrations results (Fig. 6.15). The effluent NO_3-N concentrations that were low until day 22 showed an increasing trend thereafter, as a result of oxidation of ammonia to nitrate by nitrifying bacteria. On the other hand, TKN concentrations also showed decreasing trend from 30 days and dropped below 5 mg/l after approximately 41 days. Utilization of TKN by the bacteria suggests that the nitrogen associated by organic matter can be used by microorganisms toward the nutrient requirements. This observation is in agreement with the earlier findings by A.D. Little Inc. [1], and indicates that the original wastewater has suitable nitrogenous compounds that can provide the nutrient requirement of nitrogen. Because, the TKN values for original wastewater were approximately 70 mg/l, which is the amount of nitrogen required by the biomass, there seems to be no need to supplement the wastewater with external nitrogen sources. Support for this statement can be obtained from the earlier study by A.D. Little Inc.[1], which reported no external addition of nitrogen source in treating BP wastewater. Although this was realized during the study, no attempt was made to terminate the addition of external nitrogen source, because it might upset the system stability due to impact on the nitrifying bacteria. As a result, significant production of nitrate nitrogen was observed due to the oxidation of surplus ammonia-nitrogen. Excessive nitrification caused depression of pH since the alkalinity of original wastewater was not sufficient to properly buffer the

system. Therefore, alkalinity in the form of sodium bicarbonate ($NaHCO_3$) was added to provide pH stability. Decreases in the system pH values can be seen from Appendix A-7 .

Although effluent NH_3-N concentrations dropped below detection limits after day 41, a decreasing trend in the effluent NO_3-N concentrations, not observed until day 75, shows that the lag period could be markedly different for the two genera of bacteria. From Figure 6.10, illustrating the pathway of degradation of NG, it is evident that under aerobic conditions the nitrite ion, after cleavage, would eventually be oxidized to nitrate and accumulate in the system. From a mass balance on nitrogen, 0.185 mg of NO_3-N would be generated per mg of NG destroyed. Based on the stoichiometry of ammonia nitrification to nitrate, 70 mg/l of NH_4-N that was synthetically furnished, would produce 68.6 mg/l of NO_3-N after meeting nutrient requirements of nitrifying biomass during the periods of complete nitrification, as observed after day 41 (Fig. 6.14). Influent NO_3-N concentrations (Fig. 6.15) were low in phase I, but started to increase as a result of increases in NG concentration in the influent. Influent and effluent NO_3-N concentrations were respectively the highest (25 mg/l on average) and the lowest (detection limit) during phase III due to the use of NG in BP production and establishment of a denitrifying population. Therefore, the total mass of NO_3-N entering the anoxic phase during phase III was approximately 95 mg/l. Results presented in Fig. 6.15 illustrate effluent NO_3-N being removed to below detection limit. Since no external carbon source was provided and considering that aqueous phase COD dropped below 50 mg/l (Fig 6.16) after five hours of aeration, denitrification most likely took place by consuming endogenous carbon reserves.

6.7 Alkalinity Consumption and Production

It is known that a non-growth substrate does not support cell replication [8]. Consequently, stoichiometric alkalinity requirements for degradation of NG, based on the proposed degradation mechanism by Wendt *et al.* [34] were calculated neglecting cell yield and are presented below.

$$400\ C_3H_5(NO_3)_3 + 800\ O_2 + 1200\ HCO_3^- \longrightarrow 2400\ CO_2 + 1200\ NO_2^- + 1600\ H_2O \quad (5)$$

$$1200\ NO_2^- + 3\ NH_4^+ + 12\ H_2CO_3 + 3\ HCO_3^- + 585\ O_2 \longrightarrow 3\ C_5H_7NO_2 + 9\ H_2O + 1200\ NO_3^- \quad (6)$$

Reactions (5) and (6) can be combined to yield:

$$C_3H_5(NO_3)_3 + 3.71\ O_2 + 3\ HCO_3^- + 0.0075\ NH_4^+ + 0.03\ H_2CO_3 \longrightarrow 4\ CO_2 + 0.0075\ C_5H_7NO_2 + 3\ NO_3^- + 4.02\ H_2O \quad (7)$$

Based on equation 7, for every mg of NG destroyed, 0.269 mg of bicarbonate alkalinity would be consumed producing 0.185 mg of NO_3-N. From Fig. 6.8 and 6.14, complete oxidation of NG and other nitrogenous compounds in the influent was observed after day 41. The total amount of NO_3-N entering the anoxic phase was calculated from the influent NG, NH_3-N and TKN concentrations. The amount of NO_3-N produced in the aerobic phase due to NG degradation was calculated using equation (7) for each cycle. The amount of NO_3-N generated as a result of oxidation of surplus nitrogen was calculated stoichiometrically from the influent NH_3-N and TKN concentrations for each cycle. The extent of denitrification occurring in the anoxic phase after day 41 was calculated as the difference of influent (entering anoxic phase) NO_3-N concentration, as obtained stoichiometrically, and the effluent NO_3-N concentration, measured experimentally, for

each cycle. Since approximately 3.66 mg of bicarbonate alkalinity would be produced per mg of NO_3-N reduced to nitrogen gas [31], the amount of alkalinity produced for the extent of denitrification in each cycle was determined. A mass balance on alkalinity for each cycle was performed. From this analysis, an average value of 8.35 (±2.38) mg of bicarbonate alkalinity consumption per mg of NH_3-N nitrified was obtained. This value is comparable to the literature value of 8.64 mg of bicarbonate alkalinity consumption per mg of NH_3-N nitrified [31] and verifies the stoichiometrically calculated NO_3-N production. Given that these stoichiometric relations were developed assuming no cell yield, further support for a co-metabolic degradation mechanism of NG is provided.

7. Process Modeling and Optimization

The two SBR cycle schemes adopted in the study were operated with a static fill phase (Table 5.1). As mentioned earlier, a static-fill phase is one in which no mixing and aeration would take place until the reactor is filled to the desired volume to be treated. Static-fill was used since it was observed early in the study that settling characteristics deteriorated significantly when mixing occurred during this phase. An SBR cycle with a mixed-fill phase was adopted early in the study, because it was believed that the biomass would accumulate endogenous reserves when grown under oxygen deficient conditions and utilize these storage polymers during the denitrification phase for carbon requirements. However, operating the SBR with a mixed-fill phase adversely impacted the settleability of biomass and prohibitively increased the effluent suspended solids. Increases in effluent solids resulted in concomitant increases in the effluent COD and BOD. Also, since the priority pollutants were being removed partially by biosorption, high concentrations of effluent solids caused unacceptable concentrations of these compounds in the effluent.

In general, the success of biological treatment systems is based in large measure on sedimentation efficiency. As observed above, if a regulated compound is being removed either totally or partially by biosorption, then concentration of effluent solids becomes critical in evaluating the efficiency of treatment systems. Similar to our experience, it has been reported in the literature [7, 9, 15] that the settling characteristics of SBRs are adversely impacted by fill-react phases. Typically, the shorter this phase, the better the quality of effluent. Investigators [9] found the improved sludge settleability when there is substrate tension at the beginning of the react phase. In other words, biomass grown under substrate affluent conditions has better settling properties than the one grown under substrate deficient conditions. If biomass is aerated from the beginning of fill,

simultaneous utilization prevents the build up of substrate concentration. Further, it has also been proposed that high substrate gradients control filamentous growth which often causes settling problems [9]. In essence, this suggests that static-fill rather than react-fill be employed for efficient performance of SBRs. Such a behavior may seriously handicap SBRs in treating toxic wastes because the volume of the toxic waste, such as NG laden wastes, that can be treated per cycle is limited to the toxicity threshold concentration that the biomass can safely tolerate. However, this problem can be solved by initiating aeration once the toxicity limit is approached by static-fill but continuing filling until the required volume to be treated is reached. This approach balances appropriate static-fill and react-fill phases. Once the aeration begins, the influent flow rate should be such that the rate of change of the toxic compound concentration in the reactor is either zero or negative so that the concentration remains below inhibitory levels. A model to exploit this capability to treat high concentrations of NG, or any toxic waste in general, has been developed and simulations run to investigate SBR response to transient toxic loads.

7.1 Model

In this model, it is assumed that the growth substrate and biomass are in excess and only NG concentrations are rate limiting (pseudo first order assumption):

A mass balance on the targeted compound is given by

$$\frac{d}{dt}(VC_i) = qC_o + VR \qquad (8)$$

For,

(a) the static-fill phase, substituting R = 0 and rearranging and integrating equation (8) gives

$$C_i = \frac{q\,t\,C_o}{V_{fo} + qt} \qquad (9)$$

(b) react-fill phase, assuming a first order reaction, integrating equation (8), and rearranging the terms yields

$$C_i = \frac{C_o}{(t + g_o)\,k} - \left[\frac{C_o}{g_o\,k} - C_{tox}\right]\frac{g_o}{g_o + k}\,e^{-kt} \qquad (10)$$

and,

(c) react phase, substituting q =0, rearranging and integrating equation (8) gives

$$C_i = C_o\,e^{-kt} \qquad (11)$$

where,

C_o = concentration of toxic compound in the influent (ML^{-3})

C_i = temporal toxic compound concentration in the reactor (ML^{-3})

C_{tox} = maximum allowable concentration of toxic compound in the reactor (ML^{-3})

V = temporal volume of substrate (L^3)

R = rate of removal of toxic compound (MT^{-1})

q = influent flow rate (L^3T^{-1})

k = first order rate constant (T^{-1})

$g_o = V_{ro}/q$ (T)

V_{ro} = volume of substrate at the beginning of react-fill phase (L^3)

V_{fo} = volume of substrate at the beginning of static-fill phase (L^3)

Fig. 7.1: Predicted Reactor NG Temporal Profiles without React-Fill Phase

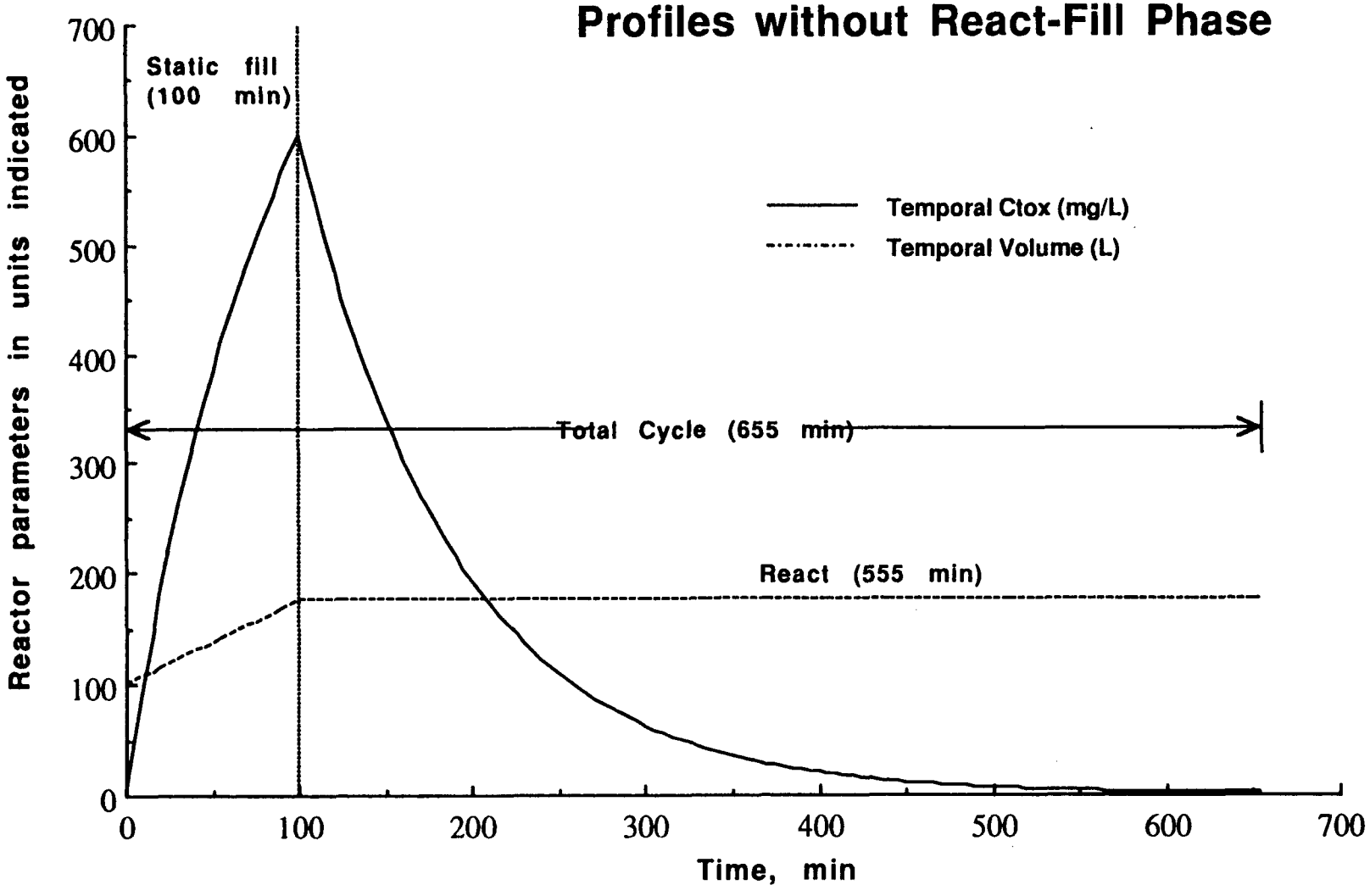
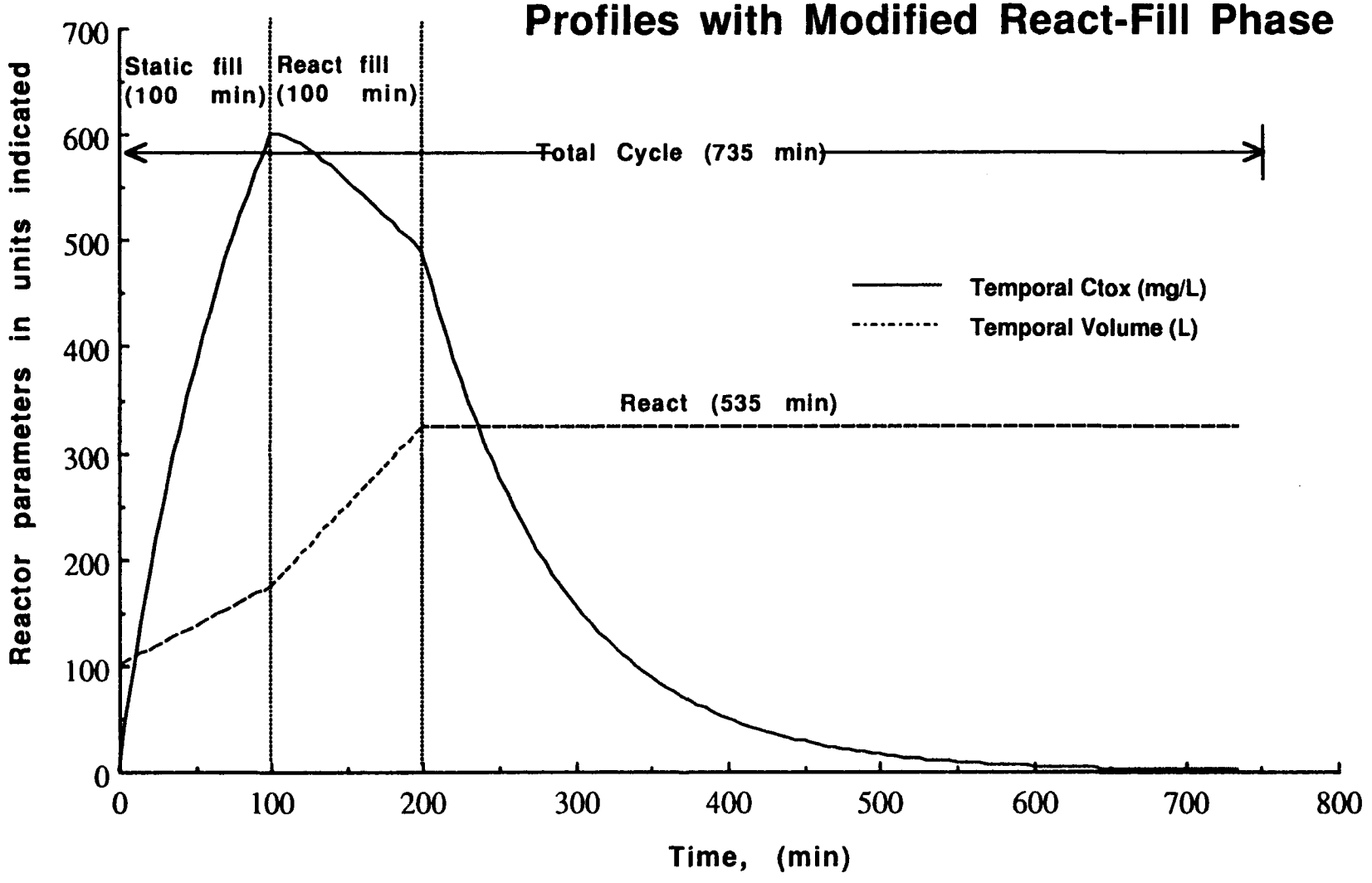


Fig. 7.2: Predicted Reactor NG Temporal Profiles with Modified React-Fill Phase



7.2 Simulations and Results

An experimentally determined first order rate constant, k, for NG was found to be 0.0114/min and the threshold toxic concentration, C_{tox}, of NG was reported to be 600 mg/l [34]. Assuming an influent NG concentration (C_0) of 1400 mg/l and an initial SBR volume (mixed liquor) of 100 liters, simulations were run to predict temporal NG profiles without (Fig 7.1) and with (Fig 7.2) react-fill phase. Fig 7.1 depicts the temporal variations of reactor volumes and NG concentrations without react-fill phase. The threshold toxic NG concentration (600 mg/l) was attained when the reactor volume approached 175 liters. Excluding the 100 liters of mixed liquor that was initially present, the maximum volume of waste that could be treated in each cycle was therefore limited to 75 liters. From this figure, the total cycle time that would be required to bring the NG concentration to approximately 1 mg/l was 655 min. If three times the volume of waste (225 liters), for example, were to be treated in this SBR system operating with no react-fill phase, it would therefore require three cycle times (i.e. 1965 min). The static-fill and react phase temporal NG concentrations of Fig 7.1 were predicted using equations (9) and (11), respectively. Fig 7.2 illustrates the case in which the SBR system is operated with both a static-fill and a react-fill phase. The static-fill, react-fill and react phase temporal NG profiles of Fig 7.2 were predicted using equations (9), (10) and (11), respectively. Since it is preferable to maintain the shortest react-fill phase in order to create high substrate tension, the influent flow rate to be adopted in the react-fill phase should be the maximum flow rate attainable without developing toxic conditions. The optimum influent flow rate in the react-fill phase was determined using equation (10) such that NG concentration was always below toxic limit ($\leq$ 600 mg/l) (Fig 7.2). Operating at the maximum allowable influent flow rate, the react-fill phase was terminated when the reactor volume approached 325 liters (Fig 7.2). From Fig 7.2, a total cycle time of 735 min is required to remove NG concentration to approximately 1 mg/L. Therefore, a volume of 225 liters (excluding 100

liters of mixed liquor) could be treated in 735 min by operating the reactor with a react-fill phase. A comparison of cycle times of the above two cases shows that approximately 63% reduction in the cycle time could be achieved in treating a given volume of waste by operating the SBR with a variable react-fill phase. Since concentrations in the reactor do not significantly drop (17%) during the react-fill phase, the substrate tension necessary for better settling characteristics of biomass could still be maintained. Clearly, appropriate and controlled use of a react-fill phase significantly extends the utility of SBR systems for the treatment of toxic compounds.

8. Conclusions and Recommendations

The primary objective of the pilot-scale study was to investigate the biodegradability of NG and its impact on the overall performance of the treatment system in terms of meeting the effluent limits. Contrary to previous findings [2], the results of pilot sale study demonstrated that NG is degradable to below detection limits in conventional treatment systems. Within the operating concentrations studied, NG was found not to be toxic and exhibited no adverse impact either on the removal of priority pollutants or in meeting effluent standards. Studies on reactor temporal NG concentrations indicated that the removal mechanism was primarily due to biodegradation and occured under aerobic conditions. While NG was found amenable to biodegradation in the presence of alternate growth supporting substrates, its recalcitrance to biodegradation when available as a sole carbon source indicated that degradation is most likely occurring via co-metabolism. The consequences of these findings are of major significance. It is clear that if stable system performance is to be realized, a sufficient primary carbon source must be available in the influent. This may require the addition of an external carbon source to supplement the influent BOD, especially if NG concentrations become excessive. The obligate presence of EA, the growth substrate, required during the transformation of NG, the co-metabolite, was insured under aerobic conditions. Loss of EA due to volatilization was found to be minimal. Since BP wastewater has sufficient organic nitrogen compounds suitable for nitrogen requirements, only phosphorous needs to be supplemented for nutrient requirements. SBR proved to be a viable treatment option for biological oxidation, nitrification, and denitrification in a single unit. The results of temporal studies on reactor NO_3-N and NG concentrations indicated that the lengths of aerobic (8 hrs) and anoxic (5 hrs) periods selected were appropriate. NH_3-N and NO_3-N concentrations were reduced to below detection limits and no external carbon source was supplied during denitrification.

Although a combined system was employed, no difficulty was encountered in meeting effluent suspended solids standards. These results can be used as a basis for the design of a full-scale treatment system. SBR cycles operated with longer fill and shorter idle phases showed a notable improvement in the effluent quality. In agreement with earlier findings [9], operating the SBR with static-fill significantly improved the settling characteristics of biomass. But a strict static-fill phase could limit the volume of a toxic waste that can be treated per cycle to the compound toxic threshold concentration that a biomass could tolerate. To alleviate this short coming, a model was proposed that could be used to properly balance static and react fill phases. Simulations were run to investigate SBR response to transient toxic load conditions, highlighting SBRs versatility in treating toxic compounds.

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APPENDIX

A-1: Influent and Effluent COD

(T = Total; S = Soluble; I = Influent; E = Effluent; NA = Not Analysed)

Date	Days After Startup	COD (T, I) mg/l	COD (S, I) mg/l	COD (S, E) mg/l	COD (T, E) mg/l
1/23/91	1	1700	1350	83	250
1/24/91	2	1434	1200	45	200
1/25/91	3	1467	1117	40	250
1/26/91	4	1517	1383	30	150
1/27/91	5	1450	1333	40	80
1/28/91	6	1150	925	35	70
1/29/91	7	965	650	35	65
1/30/91	8	1375	1150	18	55
1/31/91	9	1300	990	17	45
2/1/91	10	1100	1000	25	62
2/2/91	11	1200	1100	18	50
2/3/91	12	1350	1275	20	68
2/4/91	13	1086	1045	22	93
2/5/91	14	1225	1175	25	72
2/6/91	15	1300	1200	25	95
2/7/91	16	1550	1350	33	100
2/8/91	17	1500	1050	40	85
2/9/91	18	1400	1250	38	75
2/10/91	19	1500	1350	25	61
2/11/91	20	1487	1270	30	65
2/12/91	21	1500	1350	40	80
2/13/91	22	1450	1325	35	70
2/14/91	23	1475	1350	30	70
2/15/91	24	1500	1350	35	80
2/16/91	25	1475	1350	20	60
2/17/91	26	1500	1250	25	55
2/18/91	27	1500	1375	15	55
2/19/91	28	1400	1275	18	52
2/20/91	29	1462	1262	25	55
2/21/91	30	1500	1375	25	65
2/22/91	31	1500	1188	35	60
2/23/91	32	1750	1213	25	60
2/24/91	33	1700	900	25	50
2/25/91	34	2125	1500	40	80
2/26/91	35	1450	NA	25	65
2/27/91	36	1350	950	25	60
2/28/91	37	1525	1000	25	75
3/1/91	38	1800	1750	20	65
3/2/91	39	1550	1500	25	70

A-1 (cont..)

Date	Days After Startup	COD (T, I) mg/l	COD (S, I) mg/l	COD (S, E) mg/l	COD (T, E) mg/l
3/3/91	40	1800	1600	25	75
3/4/91	41	2188	1375	20	55
3/5/91	42	2375	1750	25	65
3/6/91	43	1600	1150	15	70
3/7/91	44	1900	1800	30	90
3/8/91	45	1900	1700	22	75
3/9/91	46	2000	1700	15	70
3/10/91	47	1700	1500	25	55
3/11/91	48	2125	NA	25	40
3/12/91	49	1975	1300	40	60
3/13/91	50	1500	1050	21	37.5
3/14/91	51	1725	1550	20	40
3/15/91	52	1550	1250	20	42
3/16/91	53	1800	1600	10	30
3/17/91	54	1600	1450	20	45
3/18/91	55	1500	1250	9	38
3/19/91	56	1600	1400	21	48
3/20/91	57	1650	1400	22	51
3/21/91	58	1700	1300	22	50
3/22/91	59	1450	900	20	40
3/23/91	60	1700	1150	14	54
3/24/91	61	1750	1250	20	50
3/25/91	62	1700	1200	15	40
3/26/91	63	1800	1400	16	40
3/27/91	64	1525	1400	15	40
3/28/91	65	1415	1315	34	55
3/29/91	66	1620	1420	20	44
3/30/91	67	1600	1350	17	42
3/31/91	68	1520	1250	10	30
4/1/91	69	1600	1250	15	35
4/2/91	70	1750	1200	15	35
4/3/91	71	1650	1180	17	36
4/4/91	72	1700	1125	20	35
4/5/91	73	1600	1150	22	50
4/6/91	74	1600	1100	12	35
4/7/91	75	1650	895	20	55
4/8/91	76	1600	775	15	75
4/9/91	77	1600	720	15	43
4/10/91	78	1600	590	24	81
4/11/91	79	1950	650	25	82

A-1 (cont..)

Date	Days After Startup	COD (T, I) mg/l	COD (S, I) mg/l	COD (S, E) mg/l	COD (T, E) mg/l
4/12/91	80	1815	500	15	80
4/13/91	81	1920	1200	20	130
4/14/91	82	1960	1200	20	35
4/15/91	83	2030	1150	30	52
4/16/91	84	2120	1225	21	53
4/17/91	85	2400	775	27	37
4/18/91	86	2030	1200	35	67
4/19/91	87	2030	1150	37	62
4/20/91	88	2000	1100	NA	NA
4/21/91	89	2020	1300	22	42
4/22/91	90	2000	1350	28	50
4/23/91	91	1990	900	20	45
4/24/91	92	1926	900	20	45
4/25/91	93	2060	1025	10	62
4/26/91	94	1400	1250	15	50
4/27/91	95	1450	1300	20	48
4/28/91	96	1575	1250	20	55
4/29/91	97	1500	1150	25	105
4/30/91	98	1500	1150	20	95
5/1/91	99	1500	1150	22	87
5/2/91	100	1500	1150	24	82
5/3/91	101	2100	1100	28	95
5/4/91	102	2195	1100	40	100
5/5/91	103	1900	1050	40	100
5/6/91	104	2000	1100	40	100
5/7/91	105	2000	1100	22	115
5/8/91	106	1900	1250	22	51
5/9/91	107	2000	1250	22	44
5/10/91	108	1800	960	22	58
5/11/91	109	2000	1250	31	67
5/12/91	110	1930	1300	40	72
5/13/91	111	1500	NA	25	65

A-2: Influent and Effluent BOD

(T = Total; S = Soluble; I = Influent; E = Effluent; NA = Not Analysed)

Date	Days After Startup	BOD (T, I) mg/l	BOD (S, I) mg/l	BOD (T, E) mg/l	BOD (S, E) mg/l
1/23/91	1	NA	NA	54	23
1/24/91	2	825	690	NA	NA
1/25/91	3	NA	NA	90	19
1/26/91	4	915	670	66	14
1/27/91	5	945	965	NA	NA
1/28/91	6	NA	NA	38	11
1/29/91	7	536	429	NA	NA
1/30/91	8	NA	NA	12	NA
1/31/91	9	825	578	NA	NA
2/1/91	10	NA	NA	26	1.5
2/2/91	11	840	780	29	0
2/3/91	12	698	555	NA	NA
2/4/91	13	NA	NA	NA	NA
2/5/91	14	NA	NA	NA	NA
2/6/91	15	NA	NA	60	0
2/7/91	16	875	785	NA	NA
2/8/91	17	NA	NA	30	6
2/9/91	18	1230	1110	20	0
2/10/91	19	773	600	NA	NA
2/11/91	20	NA	NA	NA	NA
2/12/91	21	NA	NA	NA	NA
2/13/91	22	NA	NA	32	0
2/14/91	23	833	818	NA	NA
2/15/91	24	NA	NA	31	NA
2/16/91	25	1050	1035	NA	NA
2/17/91	26	NA	NA	NA	NA
2/18/91	27	NA	NA	26	NA
2/19/91	28	923	803	NA	NA
2/20/91	29	NA	NA	NA	NA
2/21/91	30	NA	NA	NA	NA
2/22/91	31	NA	NA	10.5	2.1
2/23/91	32	960	735	NA	NA
2/24/91	33	NA	NA	NA	NA
2/25/91	34	NA	NA	17	0
2/26/91	35	2010	713	NA	NA
2/27/91	36	NA	NA	17	0
2/28/91	37	968	578	NA	NA
3/1/91	38	NA	NA	41	0
3/2/91	39	923	878	33	5

A-2 (cont..)

Date	Days After Startup	BOD (T, I) mg/l	BOD (S, I) mg/l	BOD (T, E) mg/l	BOD (S, E) mg/l
3/3/91	40	1043	885	NA	NA
3/4/91	41	NA	NA	8	2
3/5/91	42	1470	945	NA	NA
3/6/91	43	NA	NA	24	0
3/7/91	44	1290	990	NA	NA
3/8/91	45	NA	NA	52	0
3/9/91	46	1350	1215	34	0
3/10/91	47	1320	1058	NA	NA
3/11/91	48	NA	NA	13	0
3/12/91	49	960	615	NA	NA
3/13/91	50	NA	NA	14	0
3/14/91	51	1140	1110	NA	NA
3/15/91	52	NA	NA	18.5	0
3/16/91	53	720	638	14.5	0
3/17/91	54	789	720	NA	NA
3/18/91	55	NA	NA	10.5	0
3/19/91	56	NA	NA	NA	NA
3/20/91	57	NA	NA	17	5
3/21/91	58	705	638	NA	NA
3/22/91	59	NA	NA	12.5	2
3/23/91	60		510	17	1.5
3/24/91	61	1275	825	NA	NA
3/25/91	62	NA	NA	11	0
3/26/91	63		1185	12	0
3/27/91	64	1110	1110	11	0
3/28/91	65	1020	900	16.5	0
3/29/91	66	1005	742	10.5	0
3/30/91	67	1410	930	12	0
3/31/91	68	1200	945	11	10
4/1/91	69	1230	1058	10	0
4/2/91	70	1320	840	15	0
4/3/91	71	1230	1035	10	0
4/4/91	72	1395	1110	10	0
4/5/91	73	960	630	12	0
4/6/91	74	848	713	10	0
4/7/91	75	675	638	18	0
4/8/91	76	705	495	35	0
4/9/91	77	450	276	30	0
4/10/91	78	503	330	52	4
4/11/91	79	578	443	31	0

A-2 (cont..)

Date	Days After Startup	BOD (T, I) mg/l	BOD (S, I) mg/l	BOD (T, E) mg/l	BOD (S, E) mg/l
4/12/91	80	423	294	35	0.4
4/13/91	81	NA	NA	62	2
4/14/91	82	NA	NA	0	0
4/15/91	83	713	630	0	0
4/16/91	84	773	638	0	0
4/17/91	85	458	416	NA	NA
4/18/91	86	NA	NA	0	0
4/19/91	87	698	608	0	0
4/20/91	88	608	578	NA	NA
4/21/91	89	NA	NA	NA	NA
4/22/91	90	NA	NA	0	0
4/23/91	91	877	578	17	0
4/24/91	92	653	578	10	0
4/25/91	93	705	668	NA	NA
4/26/91	94	NA	NA	NA	NA
4/27/91	95	NA	NA	NA	NA
4/28/91	96	NA	NA	9	0
4/29/91	97	645	638	14	0
4/30/91	98	623	600	14	0
5/1/91	99	660	645	17	0
5/2/91	100	668	630	19	0
5/3/91	101	1140	1020	15	0
5/4/91	102	1185	1080	12.5	0
5/5/91	103	1095	990	10.5	0
5/6/91	104	1140	960	10.5	0
5/7/91	105	1065	863	NA	NA
5/8/91	106	NA	NA	NA	NA
5/9/91	107	NA	NA	0	0
5/10/91	108	1175	945	NA	NA
5/11/91	109	NA	NA	0	0
5/12/91	110	1155	803	NA	NA
5/13/91	111	NA	NA	0	0

A-3: Reactor MLVSS, Effluent TSS and F:M Ratio

(E = Effluent; F = Food (COD); M = Microorganisms; R = Reactor; NA = Not Analysed
MLVSS = Mixed Liquor Suspended Solids; TSS = Total Suspended Solids)

Date	Days After Startup	MLVSS (R) mg/l	TSS (E) mg/l	F:M mg/mg/d
1/23/91	1	1950	100	NA
1/24/91	2	2165	83	NA
1/25/91	3	3373	125	0.17
1/26/91	4	3730	95	0.16
1/27/91	5	3770	54	0.15
1/28/91	6	3880	40	0.12
1/29/91	7	3760	38	0.10
1/30/91	8	3540	20	0.16
1/31/91	9	3530	28	0.15
2/1/91	10	3510	27	0.13
2/2/91	11	3513	33	0.14
2/3/91	12	3673	30	0.15
2/4/91	13	3700	55	0.12
2/5/91	14	3530	27	0.14
2/6/91	15	3525	30	0.15
2/7/91	16	3737	40	0.17
2/8/91	17	3850	39	0.16
2/9/91	18	3685	17	0.15
2/10/91	19	3817	15	0.16
2/11/91	20	3925	17	0.15
2/12/91	21	4173	23	0.14
2/13/91	22	3931	22	0.15
2/14/91	23	3625	27	0.16
2/15/91	24	3905	17	0.15
2/16/91	25	4047	8.5	0.15
2/17/91	26	4028	20.5	0.15
2/18/91	27	3950	24	0.15
2/19/91	28	4348	26	0.13
2/20/91	29	3881	27	0.15
2/21/91	30	3596	17	0.17
2/22/91	31	3610	17	0.17
2/23/91	32	3823	13.5	0.18
2/24/91	33	3961	14	0.17
2/25/91	34	4412	16	0.19
2/26/91	35	4118	47	0.14
2/27/91	36	3822	18	0.14
2/28/91	37	4044	12	0.15
3/1/91	38	3845	13.5	0.19

A-3 (cont..)

Date	Days After Startup	MLVSS (R) mg/l	TSS (E) mg/l	F:M mg/mg
3/2/91	39	3950	12	0.16
3/3/91	40	3900	19	0.18
3/4/91	41	3837	34	NA
3/5/91	42	3948	14.5	NA
3/6/91	43	3945	14.5	0.16
3/7/91	44	3958	20	0.19
3/8/91	45	4060	14	0.19
3/9/91	46	3944	33	NA
3/10/91	47	3937	15	0.17
3/11/91	48	3741	11	NA
3/12/91	49	4385	8	0.18
3/13/91	50	4040	10	0.15
3/14/91	51	4012	10	0.17
3/15/91	52	4096	18	0.15
3/16/91	53	4090	17	0.18
3/17/91	54	4002	18	0.16
3/18/91	55	4106	20	0.15
3/19/91	56	4240	20	0.15
3/20/91	57	4036	23	0.16
3/21/91	58	4038	17	0.17
3/22/91	59	4167	17.5	0.14
3/23/91	60	3790	16	0.18
3/24/91	61	4131	15	0.17
3/25/91	62	4294	18	0.16
3/26/91	63	4701	16	0.15
3/27/91	64	4540	15	0.13
3/28/91	65	4510	14	0.13
3/29/91	66	4552	17	0.14
3/30/91	67	4453	16.5	0.14
3/31/91	68	4400	14.5	0.14
4/1/91	69	4320	12	0.15
4/2/91	70	4413	11	0.16
4/3/91	71	4205	17	0.16
4/4/91	72	4311	14.5	0.16
4/5/91	73	4211	21	0.15
4/6/91	74	4383	12	0.15
4/7/91	75	3658	13	0.18
4/8/91	76	4873	16.5	0.13
4/9/91	77	NA	29	NA
4/10/91	78	4748	11.5	0.13

A-3 (cont..)

Date	Days After Startup	MLVSS (R) mg/l	TSS (E) mg/l	F:M mg/mg
4/11/91	79	4903	15	0.16
4/12/91	80	5099	16	0.14
4/13/91	81	5103	19	0.15
4/14/91	82	NA	134	NA
4/15/91	83	5080	10.5	0.16
4/16/91	84	5270	14.5	0.16
4/17/91	85	4373	11.5	NA
4/18/91	86	NA	NA	NA
4/19/91	87	5352	16	0.15
4/20/91	88	5533		0.14
4/21/91	89	NA	NA	NA
4/22/91	90		NA	0.19
4/23/91	91	5326	29.5	0.15
4/24/91	92	5269	20.5	0.15
4/25/91	93	5319	17	0.15
4/26/91	94	5125	28	0.11
4/27/91	95	5735	31	0.10
4/28/91	96	5729	17	0.11
4/29/91	97	5216	31	0.12
4/30/91	98	4421	61	0.14
5/1/91	99	3995	64	0.15
5/2/91	100	4034	69	0.15
5/3/91	101	4091	27.5	NA
5/4/91	102	4106	30.5	NA
5/5/91	103	4659	42	0.16
5/6/91	104	4390	49	0.18
5/7/91	105	4622	41	0.17
5/8/91	106	5230	60	0.15
5/9/91	107	5279	28	0.15
5/10/91	108	5632	16	0.13
5/11/91	109	5600	27	0.14
5/12/91	110	5583	28	0.14
5/13/91	111	NA	29	NA

A-4 : Influent, Effluent and Sludge NG

(I* = Influent (spiked); I** = Influent (measured); E = Effluent; S = Sludge; NA = Not Analysed)

Date	Days After Startup	NG(I)* ug/l	NG(I)** ug/l	NG(E) ug/l	NG(S) ug/Kg
1/23/91	1	NA	896	5	5
1/24/91	2	NA	5	NA	NA
1/25/91	3	NA	NA	NA	NA
1/26/91	4	NA	NA	NA	NA
1/27/91	5	NA	NA	NA	NA
1/28/91	6	NA	NA	5	62.2
1/29/91	7	NA	402	5	63.9
1/30/91	8	NA	6.27	5	33.6
1/31/91	9	NA	19.4	NA	NA
2/1/91	10	NA	NA	NA	NA
2/2/91	11	NA	NA	NA	NA
2/3/91	12	NA	NA	NA	NA
2/4/91	13	NA	NA	5	118
2/5/91	14	NA	5	5	52.8
2/6/91	15	NA	5	5	25.9
2/7/91	16	NA	5	NA	NA
2/8/91	17	NA	NA	NA	NA
2/9/91	18	NA	NA	NA	NA
2/10/91	19	NA	NA	NA	NA
2/11/91	20	2000	NA	21.2	63.4
2/12/91	21	2000	5	5	19.7
2/13/91	22	2000	1170	5	52.6
2/14/91	23	2000	1600	NA	NA
2/15/91	24	5000	NA	NA	NA
2/16/91	25	5000	NA	NA	NA
2/17/91	26	5000	NA	NA	NA
2/18/91	27	5000	NA	5	165
2/19/91	28	5000	552	5	131
2/20/91	29	8000	1340	5	NA
2/21/91	30	8000	1580	NA	NA
2/22/91	31	8000	NA	NA	NA
2/23/91	32	8000	NA	5	98.9
2/24/91	33	8000	1870	NA	NA
2/25/91	34	12000	NA	NA	NA
2/26/91	35	12000	928	5	89.6
2/27/91	36	12000	NA	NA	NA
2/28/91	37	12000	1040	6.75	43.1
3/1/91	38	12000	NA	NA	NA
3/2/91	39	18000	NA	NA	NA

A-4 (cont..)

Date	Days After Startup	NG(I)* ug/l	NG(I)** ug/l	NG(E) ug/l	NG(S) ug/Kg
3/3/91	40	18000	NA	5	16.9
3/4/91	41	18000	10200	5	5
3/5/91	42	18000	6600	NA	NA
3/6/91	43	25000	NA	5	30
3/7/91	44	25000	22400	NA	NA
3/8/91	45	25000	NA	NA	NA
3/9/91	46	25000	NA	NA	NA
3/10/91	47	35000	NA	NA	594
3/11/91	48	35000	NA	NA	NA
3/12/91	49	35000	NA	5	645
3/13/91	50	35000	7720	NA	NA
3/14/91	51	35000	8410	NA	770
3/15/91	52	45000	NA	NA	NA
3/16/91	53	45000	NA	5	35.5
3/17/91	54	45000	15000	NA	NA
3/18/91	55	45000	NA	5	36.1
3/19/91	56	45000	16200	NA	NA
3/20/91	57	55000	NA	5	43.9
3/21/91	58	55000	31800	NA	NA
3/22/91	59	55000	NA	NA	NA
3/23/91	60	55000	NA	5	477
3/24/91	61	55000	18700	NA	NA
3/25/91	62	70000	NA	NA	NA
3/26/91	63	70000	53800	NA	NA
3/27/91	64	70000	NA	NA	NA
3/28/91	65	90000	NA	5	16000
3/29/91	66	90000	46300	NA	NA
3/30/91	67	90000	NA	NA	NA
3/31/91	68	90000	NA	5	6210
4/1/91	69	90000	67100	NA	NA
4/2/91	70	90000	NA	5	12200
4/3/91	71	120000	75200	NA	NA
4/4/91	72	120000	NA	8.13	16700
4/5/91	73	120000	89600	NA	NA
4/6/91	74	120000	NA	NA	NA
4/7/91	75	160000	NA	5	13900
4/8/91	76	160000	110000	NA	NA
4/9/91	77	160000	NA	5	12800
4/10/91	78	160000	NA	NA	NA
4/11/91	79	160000	NA	5	5620

A-4 (cont..)

Date	Days After Startup	NG(I)* ug/l	NG(I)** ug/l	NG(E) ug/l	NG(S) ug/Kg
4/12/91	80	160000	NA	NA	NA
4/13/91	81	NA	141000	NA	NA
4/14/91	82	NA	NA	6.67	NA
4/15/91	83	NA	NA	NA	NA
4/16/91	84	NA	NA	5	8985
4/17/91	85	NA	NA	NA	NA
4/18/91	86	NA	NA	NA	NA
4/19/91	87	NA	NA	NA	NA
4/20/91	88	NA	NA	NA	NA
4/21/91	89	NA	NA	5	10600
4/22/91	90	NA	NA	NA	NA
4/23/91	91	NA	NA	5	4110
4/24/91	92	NA	NA	NA	NA
4/25/91	93	NA	NA	5	NA
4/26/91	94	NA	169000	NA	NA
4/27/91	95	NA	NA	NA	NA
4/28/91	96	NA	NA	5	NA
4/29/91	97	NA	NA	NA	NA
4/30/91	98	NA	NA	5	NA
5/1/91	99	NA	NA	NA	NA
5/2/91	100	NA	NA	5	7890
5/3/91	101	NA	NA	NA	NA
5/4/91	102	NA	NA	NA	NA
5/5/91	103	NA	NA	5	6480
5/6/91	104	NA	NA	NA	NA
5/7/91	105	NA	NA	NA	NA
5/8/91	106	NA	NA	5	NA
5/9/91	107	NA	NA	5	NA
5/10/91	108	NA	205000	NA	NA
5/11/91	109	NA	NA	NA	NA
5/12/91	110	NA	NA	5	NA
5/13/91	111	NA	NA	NA	NA

A-5: Influent, Effluent and Sludge DBP

(I = Influent; E = Effluent; S = Sludge; NA = Not Analysed)

Date	Days After Startup	DBP (I) ug/l	DBP (E) ug/l	DBP (S) ug/Kg
1/23/91	1	1220	72.7	54.8
1/24/91	2	904	NA	NA
1/25/91	3	NA	NA	NA
1/26/91	4	NA	NA	NA
1/27/91	5	NA	NA	NA
1/28/91	6	NA	5	24.4
1/29/91	7	330	5	36.3
1/30/91	8	612	5	14.8
1/31/91	9	686	NA	NA
2/1/91	10	NA	NA	NA
2/2/91	11	NA	NA	NA
2/3/91	12	NA	NA	NA
2/4/91	13	NA	5	61.4
2/5/91	14	2090	5	43.3
2/6/91	15	1530	5	55
2/7/91	16	2280	NA	NA
2/8/91	17	NA	NA	NA
2/9/91	18	NA	NA	NA
2/10/91	19	NA	NA	NA
2/11/91	20	NA	5	35.9
2/12/91	21	2090	5	34.3
2/13/91	22	1990	5	94.7
2/14/91	23	2030	NA	NA
2/15/91	24	NA	NA	NA
2/16/91	25	NA	NA	NA
2/17/91	26	NA	NA	NA
2/18/91	27	NA	5	109
2/19/91	28	211	5	53.9
2/20/91	29	35	5	NA
2/21/91	30	109	NA	NA
2/22/91	31	NA	NA	NA
2/23/91	32	NA	5	32.2
2/24/91	33	19.4	NA	NA
2/25/91	34	NA	NA	NA
2/26/91	35	19.6	5	24.7
2/27/91	36	NA	NA	NA
2/28/91	37	24.4	5	28.6
3/1/91	38	NA	NA	NA
3/2/91	39	NA	NA	NA

A-5 (cont..)

Date	Days After Startup	DBP (I) ug/l	DBP (E) ug/l	DBP (S) ug/Kg
3/3/91	40	545	5	39.8
3/4/91	41	NA	NA	NA
3/5/91	42	215	5	29
3/6/91	43	NA	NA	NA
3/7/91	44	1070	5	42.7
3/8/91	45	NA	NA	NA
3/9/91	46	NA	NA	NA
3/10/91	47	114	5	13900
3/11/91	48	NA	NA	NA
3/12/91	49	216	5	16900
3/13/91	50	NA	NA	NA
3/14/91	51		5	13900
3/15/91	52	NA	NA	NA
3/16/91	53	NA	NA	NA
3/17/91	54	401	5	3970
3/18/91	55	NA	NA	NA
3/19/91	56	515	5	3800
3/20/91	57		NA	NA
3/21/91	58	342	5	4880
3/22/91	59	NA	NA	NA
3/23/91	60	NA	NA	NA
3/24/91	61	522	5	14800
3/25/91	62	NA	NA	NA
3/26/91	63	637	5	14100
3/27/91	64	NA	NA	NA
3/28/91	65	373	5	27000
3/29/91	66	NA	NA	NA
3/30/91	67	NA	NA	NA
3/31/91	68	109	5	28300
4/1/91	69	NA	NA	NA
4/2/91	70	602	5	29900
4/3/91	71	NA	NA	NA
4/4/91	72	218	5	37500
4/5/91	73	NA	NA	NA
4/6/91	74	NA	NA	NA
4/7/91	75	521	9.7	16100
4/8/91	76	NA	NA	NA
4/9/91	77	NA	5	6340
4/10/91	78	NA	NA	NA
4/11/91	79	NA	NA	4020

A-5 (cont..)

Date	Days After Startup	DBP (I) ug/l	DBP (E) ug/l	DBP (S) ug/Kg
4/12/91	80	NA	NA	NA
4/13/91	81	1287	NA	NA
4/14/91	82	NA	6.67	NA
4/15/91	83	NA	NA	NA
4/16/91	84	NA	5	7130
4/17/91	85	NA	NA	NA
4/18/91	86	NA	NA	NA
4/19/91	87	NA	NA	NA
4/20/91	88	NA	NA	NA
4/21/91	89	NA	5	20700
4/22/91	90	NA	NA	
4/23/91	91	NA	5	21200
4/24/91	92	NA	NA	NA
4/25/91	93	NA	5	NA
4/26/91	94	1060	NA	NA
4/27/91	95	NA	NA	NA
4/28/91	96	NA	5	NA
4/29/91	97	NA	NA	NA
4/30/91	98	NA	NA	NA
5/1/91	99	NA	NA	NA
5/2/91	100	NA	NA	NA
5/3/91	101	NA	5	NA
5/4/91	102	NA	NA	NA
5/5/91	103	NA	5	NA
5/6/91	104	NA	NA	NA
5/7/91	105	NA	5	NA
5/8/91	106	NA	NA	NA
5/9/91	107	NA	5	NA
5/10/91	108	7770	NA	NA
5/11/91	109	NA	NA	NA
5/12/91	110	NA	5	NA
5/13/91	111	NA	NA	NA

A-6: Influent, Effluent and Sludge DPA

(I = Influent; E = Effluent; S = Sludge; NA = Not Analysed)

Date	Days After Startup	DPA (I) ug/l	DPA (E) ug/l	DPA (S) ug/Kg
1/23/91	1	2290	381	577
1/24/91	2	2180	NA	NA
1/25/91	3	NA	NA	NA
1/26/91	4	NA	NA	NA
1/27/91	5	NA	NA	NA
1/28/91	6	NA	5	10.6
1/29/91	7	1870	5	15.6
1/30/91	8	1920	5	15.3
1/31/91	9	1930	NA	NA
2/1/91	10	NA	NA	NA
2/2/91	11	NA	NA	NA
2/3/91	12	NA	NA	NA
2/4/91	13	NA	5	31.7
2/5/91	14	2460	5	22.6
2/6/91	15	2490	5	26.7
2/7/91	16	2520	NA	NA
2/8/91	17	NA	NA	NA
2/9/91	18	NA	NA	NA
2/10/91	19	NA	NA	NA
2/11/91	20	NA	5	17.2
2/12/91	21	2870	5	15.9
2/13/91	22	2270	5	28.5
2/14/91	23	2380	NA	NA
2/15/91	24	NA	NA	NA
2/16/91	25	NA	NA	NA
2/17/91	26	NA	NA	NA
2/18/91	27	NA	5	28.1
2/19/91	28	4200	5	14.3
2/20/91	29	3620	5	NA
2/21/91	30	3970	NA	NA
2/22/91	31	NA	NA	NA
2/23/91	32	NA	5	12.3
2/24/91	33	2860	NA	NA
2/25/91	34	NA	NA	NA
2/26/91	35	2740	5	12
2/27/91	36	NA	NA	NA
2/28/91	37	2490	5	14.6
3/1/91	38	NA	NA	NA
3/2/91	39	NA	NA	NA

A-6 (cont..)

Date	Days After Startup	DPA(I) ug/l	DPA(E) ug/l	DPA(S) ug/Kg
3/3/91	40	2170	5	218
3/4/91	41	NA	NA	NA
3/5/91	42	1940	5	7.38
3/6/91	43	NA	NA	NA
3/7/91	44	2180	5	13.8
3/8/91	45	NA	NA	NA
3/9/91	46	NA	NA	NA
3/10/91	47	1770	5	2570
3/11/91	48	NA	NA	NA
3/12/91	49	2000	5	2940
3/13/91	50	NA	NA	NA
3/14/91	51	1730	5	4250
3/15/91	52	NA	NA	NA
3/16/91	53	NA	NA	NA
3/17/91	54	1300	5	1190
3/18/91	55	NA	NA	NA
3/19/91	56	1590	5	1110
3/20/91	57	NA	NA	NA
3/21/91	58	1300	5	1420
3/22/91	59	NA	NA	NA
3/23/91	60	NA	NA	NA
3/24/91	61	796	5	4840
3/25/91	62	NA	NA	NA
3/26/91	63	776	5	4010
3/27/91	64	NA	NA	NA
3/28/91	65	796	5	7890
3/29/91	66	NA	NA	NA
3/30/91	67	NA	NA	NA
3/31/91	68	917	5	2550
4/1/91	69	NA	NA	NA
4/2/91	70	NA	5	2490
4/3/91	71	NA	NA	NA
4/4/91	72	1080	5	3050
4/5/91	73	NA	NA	NA
4/6/91	74	NA	NA	NA
4/7/91	75	409	20.7	4160
4/8/91	76	NA	NA	NA
4/9/91	77	NA	5	1110
4/10/91	78	NA	NA	NA
4/11/91	79	NA	NA	746

A-6 (cont..)

Date	Days After Startup	DPA(I) ug/l	DPA(E) ug/l	DPA(S) ug/Kg
4/12/91	80	NA	NA	NA
4/13/91	81	2350	NA	NA
4/14/91	82	NA	6.67	NA
4/15/91	83	NA	NA	NA
4/16/91	84	NA	5	2581
4/17/91	85	NA	NA	NA
4/18/91	86	NA	NA	NA
4/19/91	87	NA	NA	NA
4/20/91	88	NA	NA	NA
4/21/91	89	NA	5	5540
4/22/91	90	NA	NA	NA
4/23/91	91	NA	5	4800
4/24/91	92	NA	NA	NA
4/25/91	93	NA	5	NA
4/26/91	94	1960	NA	NA
4/27/91	95	NA	NA	NA
4/28/91	96	NA	5	NA
4/29/91	97	NA	NA	NA
4/30/91	98	NA	5	NA
5/1/91	99	NA	NA	NA
5/2/91	100	NA	5	NA
5/3/91	101	NA	NA	NA
5/4/91	102	NA	7.2	NA
5/5/91	103	NA	NA	NA
5/6/91	104	NA	5	NA
5/7/91	105	NA	NA	NA
5/8/91	106	NA	NA	NA
5/9/91	107	NA	5	NA
5/10/91	108	2030	NA	NA
5/11/91	109	NA	NA	NA
5/12/91	110	NA	9.28	NA
5/13/91	111	NA	NA	NA

A-7: Influent, Effluent and Sludge 2-N-DPA

(I = Influent; E = Effluent; S = Sludge; NA = Not Analysed)

Date	Days After Startup	2-N-DPA (I) ug/l	2-N-DPA (E) ug/l	2-N-DPA (S) ug/Kg
1/23/91	1	108	19.7	11
1/24/91	2	85.1	NA	NA
1/25/91	3	NA	NA	NA
1/26/91	4	NA	NA	NA
1/27/91	5	NA	NA	NA
1/28/91	6	NA	5	5
1/29/91	7	6.71	5	5
1/30/91	8	66.9	5	5
1/31/91	9	6.23	NA	NA
2/1/91	10	NA	NA	NA
2/2/91	11	NA	NA	NA
2/3/91	12	NA	NA	NA
2/4/91	13	NA	5	6.32
2/5/91	14	85.3	5	5
2/6/91	15	74.4	5	5
2/7/91	16	60.7	NA	NA
2/8/91	17	NA	NA	NA
2/9/91	18	NA	NA	NA
2/10/91	19	NA	NA	NA
2/11/91	20	NA	5	5.11
2/12/91	21	82.2	5	5
2/13/91	22	88.3	5	5.28
2/14/91	23	84.3	NA	NA
2/15/91	24	NA	NA	NA
2/16/91	25	NA	NA	NA
2/17/91	26	NA	NA	NA
2/18/91	27	NA	5	5.5
2/19/91	28	69	5	5
2/20/91	29	51	5	NA
2/21/91	30	62.2	NA	NA
2/22/91	31	NA	NA	NA
2/23/91	32	NA	5	5
2/24/91	33	19.3	NA	NA
2/25/91	34	NA	NA	NA
2/26/91	35	22.8	5	5
2/27/91	36	NA	NA	NA
2/28/91	37	40.4	5	5
3/1/91	38	NA	NA	NA
3/2/91	39	NA	NA	NA

A-7 (cont..)

Date	Days After Startup	2-N-DPA (I) ug/l	2-N-DPA (E) ug/l	2-N-DPA (S) ug/Kg
3/3/91	40	87.1	5	5
3/4/91	41	NA	NA	NA
3/5/91	42	102	5	5
3/6/91	43	NA	NA	NA
3/7/91	44	176	5	5
3/8/91	45	NA	NA	NA
3/9/91	46	NA	NA	NA
3/10/91	47	42.9	5	173
3/11/91	48	NA	NA	NA
3/12/91	49	48.5	5	188
3/13/91	50	NA	NA	NA
3/14/91	51	12.5	5	224
3/15/91	52	NA	NA	NA
3/16/91	53	NA	NA	NA
3/17/91	54	80.1	5	35.5
3/18/91	55	NA	NA	NA
3/19/91	56	61.1	11.1	14.1
3/20/91	57	NA	NA	NA
3/21/91	58	62.3	5	17.2
3/22/91	59	NA	NA	NA
3/23/91	60	NA	NA	NA
3/24/91	61	37	5	185
3/25/91	62	NA	NA	NA
3/26/91	63	72.9	5	325
3/27/91	64	NA	NA	NA
3/28/91	65	82.3	5	157
3/29/91	66	NA	NA	NA
3/30/91	67	NA	NA	NA
3/31/91	68	180	5	817
4/1/91	69	NA	NA	NA
4/2/91	70	151	5	597
4/3/91	71	NA	NA	NA
4/4/91	72	125	5	1850
4/5/91	73	NA	NA	NA
4/6/91	74	NA	NA	NA
4/7/91	75	28.8	5	1390
4/8/91	76	NA	NA	NA
4/9/91	77	NA	5	2390
4/10/91	78	NA	NA	NA
4/11/91	79	NA	8.9	608

A-7 (cont..)

Date	Days After Startup	2-N-DPA (I) ug/l	2-N-DPA (E) ug/l	2-N-DPA (S) ug/Kg
4/12/91	80	NA	NA	NA
4/13/91	81	639	NA	NA
4/14/91	82	NA	6.67	NA
4/15/91	83	NA	NA	NA
4/16/91	84	NA	5	2528
4/17/91	85	NA	NA	NA
4/18/91	86	NA	NA	NA
4/19/91	87	NA	NA	NA
4/20/91	88	NA	NA	NA
4/21/91	89	NA	5	968
4/22/91	90	NA	NA	NA
4/23/91	91	NA	5	1420
4/24/91	92	NA	NA	NA
4/25/91	93	NA	5	NA
4/26/91	94	476	NA	NA
4/27/91	95	NA	NA	NA
4/28/91	96	NA	5	NA
4/29/91	97	NA	NA	NA
4/30/91	98	NA	NA	NA
5/1/91	99	NA	NA	NA
5/2/91	100	NA	5	NA
5/3/91	101	NA	NA	NA
5/4/91	102	NA	NA	NA
5/5/91	103	NA	9.7	NA
5/6/91	104	NA	NA	NA
5/7/91	105	NA	5	NA
5/8/91	106	NA	NA	NA
5/9/91	107	NA	5	NA
5/10/91	108	773	NA	NA
5/11/91	109	NA	NA	NA
5/12/91	110	NA	10.6	NA
5/13/91	111	NA	NA	NA

A-8: Influent & Effluent pH and Alkalinity

(I = Influent; E = Effluent; NA = Not Analysed)

Date	Days After Startup	Alkalinity (I) mg/l as CaCO3	Alkalinity (E) mg/l as CaCO3	pH (I)	pH (E)
1/23/91	1	258	336	6.3	7.3
1/24/91	2	224	NA	6.1	7.1
1/25/91	3	NA	NA	6.8	7.0
1/26/91	4	NA	NA	6.7	7.0
1/27/91	5	NA	134	6.4	6.9
1/28/91	6	325	90	6.4	6.9
1/29/91	7	314	123	6.3	6.8
1/30/91	8	190	146	6.0	7.0
1/31/91	9	202	112	6.6	6.9
2/1/91	10	190	NA	6.9	7.3
2/2/91	11	NA	NA	6.7	7.2
2/3/91	12	NA	123	7.3	7.1
2/4/91	13	280	112	6.8	7.2
2/5/91	14	246	101	6.9	7.1
2/6/91	15	258	134	6.9	7.5
2/7/91	16	213	179	6.5	6.7
2/8/91	17	314	NA	6.1	7.2
2/9/91	18	NA	NA	6.9	7.4
2/10/91	19	NA	134	6.9	7.3
2/11/91	20	246	157	7.0	7.3
2/12/91	21	269	165	6.8	7.3
2/13/91	22	278	278	6.9	7.5
2/14/91	23	268	247	6.7	7.5
2/15/91	24	288	NA	6.9	7.8
2/16/91	25	NA	NA	6.8	NA
2/17/91	26	NA	258	6.7	NA
2/18/91	27	299	216	6.8	7.4
2/19/91	28	299	246	6.9	7.4
2/20/91	29	299	247	6.7	7.8
2/21/91	30	340	268	NA	7.4
2/22/91	31	371	NA	6.7	7.8
2/23/91	32	NA	NA	6.8	7.4
2/24/91	33	NA	155	6.8	7.2
2/25/91	34	371	299	6.8	7.5
2/26/91	35	515	185	6.8	7.5
2/27/91	36	515	NA	7.1	6.5
2/28/91	37	299	31	6.8	6.1
3/1/91	38	216	NA	6.9	6.0
3/2/91	39	NA	NA	7.5	6.0

A-8 (cont..)

Date	Days After Startup	Alkalinity (I) mg/l as CaCO3	Alkalinity (E) mg/l as CaCO3	pH (I)	pH (E)
3/3/91	40	NA	5.2	7.8	5.6
3/4/91	41	1971	525	6.9	7.8
3/5/91	42	1570	1014	6.8	NA
3/6/91	43	1799	1186	NA	8.4
3/7/91	44	2153	1232	7.7	8.5
3/8/91	45	1841	NA	NA	8.4
3/9/91	46	NA	NA	NA	8.5
3/10/91	47	NA	1288	7.1	8.5
3/11/91	48	1022	984	6.9	8.2
3/12/91	49	1043	852	7.5	8.1
3/13/91	50	1398	969	7.4	8.3
3/14/91	51	924	NA	7.8	8.3
3/15/91	52	NA	861	7.6	8.3
3/16/91	53	845	NA	7.4	8.2
3/17/91	54	NA	653	7.1	8.0
3/18/91	55	823	581	7.4	8.0
3/19/91	56	810	562	7.4	8.0
3/20/91	57	725	547	7.3	7.8
3/21/91	58	723	477	7.5	8.0
3/22/91	59	697	475	7.0	8.0
3/23/91	60	NA	466	7.5	7.8
3/24/91	61	647	NA	7.5	7.8
3/25/91	62	NA	462	7.4	7.7
3/26/91	63	742	493	7.5	7.7
3/27/91	64	783	485	7.7	7.8
3/28/91	65	771	440	8.3	7.8
3/29/91	66	781	414	8.2	7.8
3/30/91	67	758	400	7.2	7.6
3/31/91	68	795	405	7.2	7.6
4/1/91	69	776	409	7.2	7.4
4/2/91	70	932	513	7.2	7.5
4/3/91	71	824	460	7.0	7.6
4/4/91	72	826	456	7.5	8.0
4/5/91	73	791	404	7.3	7.8
4/6/91	74	800	414	7.3	7.6
4/7/91	75	814	428	7.2	7.9
4/8/91	76	851	428	7.6	7.5
4/9/91	77	NA	381	8.1	7.7
4/10/91	78	851	395	7.3	7.9
4/11/91	79	846	325	7.7	8.0

A-8 (cont..)

Date	Days After Startup	Alkalinity (I) mg/l as CaCO3	Alkalinity (E) mg/l as CaCO3	pH (I)	pH (E)
4/12/91	80	860	381	7.6	8.0
4/13/91	81	804	493	7.3	8.0
4/14/91	82	NA	442	7.4	7.9
4/15/91	83	832	400	7.6	7.7
4/16/91	84	757	418	7.3	7.9
4/17/91	85	733	376	7.3	7.9
4/18/91	86	814	423	7.3	8.0
4/19/91	87	731	353	7.0	8.0
4/20/91	88	784	NA	7.1	NA
4/21/91	89	NA	321	7.1	7.6
4/22/91	90	297	297	6.6	7.5
4/23/91	91	214	279	6.6	7.5
4/24/91	92	223	279	6.6	7.6
4/25/91	93	223	246	6.6	7.5
4/26/91	94	237	NA	7.2	7.5
4/27/91	95	NA	NA	7.2	7.3
4/28/91	96	NA	205	7.3	7.3
4/29/91	97	242	200	NA	7.4
4/30/91	98	237	209	7.4	7.3
5/1/91	99	232	186	7.2	7.3
5/2/91	100	177	209	7.2	7.6
5/3/91	101	274	191	7.3	7.5
5/4/91	102	650	209	7.1	7.4
5/5/91	103	711	228	7.4	7.8
5/6/91	104	673	311	7.4	8.0
5/7/91	105	528	311	7.5	NA
5/8/91	106	NA	NA	NA	7.8
5/9/91	107	NA	353	7.0	8.2
5/10/91	108	352	335	7.1	8.1
5/11/91	109	398	288	7.6	7.8
5/12/91	110	629	NA	7.7	7.8
5/13/91	111	NA	NA	6.9	8.1

A-9: Data for BOD Assay-1

Specimen	Volume of Sample, ml	Seed ml	Initial DO mg/L	Final DO mg/L	BOD mg/l
Aerated Water	300	0.0	8.8	8.4	0.0
Dilution Water	300	0.0	8.0	7.8	0.0
Standard	6.0	6.0	8.1	4.1	190
Spiked with 200 mg/l NG	0.1	6.0	8.0	7.9	0.0
	0.5	6.0	8.0	7.9	0.0
	1.0	6.0	8.1	8.1	0.0
	0.1	6.0	8.1	8.0	0.0
	0.5	6.0	8.1	8.1	0.0
	1.0	6.0	8.0	8.0	0.0
	0.1	6.0	8.0	8.0	0.0
	0.5	6.0	8.1	8.0	0.0
	1.0	6.0	8.1	8.0	0.0
Spiked with 450 mg/l EA	2.0	6.0	8.1	4.3	540
	2.0	6.0	8.1	4.5	510
	2.0	6.0	8.1	4.1	570
	2.0	6.0	8.2	4.7	495
	2.0	6.0	8.2	4.6	510
	2.0	6.0	8.1	4.6	495
	2.0	6.0	8.2	4.8	480
	2.0	6.0	8.2	4.7	495
Spiked with 200 mg/l NG and 450 mg/l EA	2.0	6.0	8.2	4.8	480
	2.0	6.0	8.1	4.7	510
	2.0	6.0	8.0	4.4	495
	2.0	6.0	8.1	4.6	480
	2.0	6.0	8.1	4.7	480
	2.0	6.0	8.1	4.7	480
	2.0	6.0	8.2	4.8	480
	2.0	6.0	8.1	4.7	480

A-10: Data for BOD Assay-2

Specimen	Volume of Sample, ml	Seed ml	Initial DO mg/L	Final DO mg/L	BOD mg/l
Aerated Water	300	0.0	8.2	7.9	0.0
Dilution Water	300	0.0	8.5	8.2	0.0
Standard	6.0	3.0	8.5	4.4	190
Spiked with 200 mg/l NG	1.0	3.0	8.5	8.2	0.0
	3.0	3.0	8.5	8.2	0.0
	7.0	3.0	8.5	8.1	0.0
	12	3.0	8.6	8.1	0.0
	20	3.0	8.6	8.1	0.0
	30	3.0	8.6	8.0	0.0
	40	3.0	8.5	8.0	0.0
	1.0	6.0	8.5	8.1	0.0
	3.0	6.0	8.6	8.1	0.0
	7.0	6.0	8.6	8	0.0
	12	6.0	8.6	7.9	0.0
	20	6.0	8.6	7.9	0.0
	30	6.0	8.6	7.9	0.0
	40	6.0	8.5	8.1	0.0

A-11: Influent & Effluent Nitrogen

(I = Influent; E = Effluent; NA = Not Analysed)

Date	Days After Startup	NH3-N (I) mg/l	NH3-N (E) mg/l	NO3-N (I) mg/l	NO3-N (E) mg/l
1/23/91	1	95	62	0.8	0.3
1/24/91	2	95	35	0.4	0.2
1/25/91	3	89	NA	0.5	NA
1/26/91	4	NA	NA	NA	NA
1/27/91	5	NA	15	NA	0.2
1/28/91	6	81	8	0.2	0.5
1/29/91	7	104	16	0.1	0.8
1/30/91	8	NA	16	0.3	0.3
1/31/91	9	68	15	0.2	0.6
2/1/91	10	58	NA	0.2	NA
2/2/91	11	NA	NA	NA	NA
2/3/91	12	NA	111	NA	0.5
2/4/91	13	190	101	0.3	0.8
2/5/91	14	157	228	0.3	0.8
2/6/91	15	159	108	0.3	13.1
2/7/91	16	389	122	0.4	10.6
2/8/91	17	133	NA	0.4	NA
2/9/91	18	NA	NA	NA	NA
2/10/91	19	NA	123	NA	9.8
2/11/91	20	174	138	0.4	11.4
2/12/91	21	158	132	0.5	9.5
2/13/91	22	125	127	0.5	4
2/14/91	23	102	113	0.6	5.2
2/15/91	24	92	NA	0.6	NA
2/16/91	25	NA	NA	NA	NA
2/17/91	26	NA	120	NA	6
2/18/91	27	105	111	0.1	10.6
2/19/91	28	84	101	0.5	14.1
2/20/91	29	116	96	0.4	11.1
2/21/91	30	86	73	0.2	15.5
2/22/91	31	99	NA	0.5	NA
2/23/91	32	NA	NA	NA	NA
2/24/91	33	NA	45	NA	13
2/25/91	34	97	60	2	26
2/26/91	35	131	55	1.6	37
2/27/91	36	107	48	2	43
2/28/91	37	95	39	1.5	44
3/1/91	38	81	NA	1.5	NA
3/2/91	39	NA	NA	NA	NA

A-11 (cont..)

Date	Days After Startup	NH3-N (I) mg/l	NH3-N (E) mg/l	NO3-N (I) mg/l	NO3-N (E) mg/l
3/3/91	40	NA	14	NA	47
3/4/91	41	76	1	0.8	52
3/5/91	42	61	1	0.7	35
3/6/91	43	76	1.4	0.9	38.1
3/7/91	44	80	1	NA	NA
3/8/91	45	82	NA	NA	NA
3/9/91	46	NA	NA	NA	NA
3/10/91	47	NA	NA	NA	36
3/11/91	48	NA	2	3.5	29.7
3/12/91	49	89	1	3.4	29.3
3/13/91	50	77	1	3.8	36.6
3/14/91	51	70	1	0.65	34.9
3/15/91	52	77	1	1	NA
3/16/91	53	89	NA	NA	NA
3/17/91	54	NA	1	NA	34
3/18/91	55	81	1	0.9	37
3/19/91	56	76	1	1.47	37.5
3/20/91	57	74	1	0.8	37.4
3/21/91	58	69	1	0.7	53
3/22/91	59	84	NA	0.8	NA
3/23/91	60	NA	2	NA	NA
3/24/91	61	104	1	NA	43
3/25/91	62	89	1	1.4	36
3/26/91	63	87	1	1.5	26.5
3/27/91	64	85	1	5	29.1
3/28/91	65	88	2	9.2	40
3/29/91	66	79	1	8.9	NA
3/30/91	67	NA	NA	NA	NA
3/31/91	68	NA	1	NA	40.5
4/1/91	69	76	1	7.7	29
4/2/91	70	84	1	7.8	21.7
4/3/91	71	75	1.1	10.2	36.3
4/4/91	72	77	1	17.2	35.1
4/5/91	73	75	NA	NA	NA
4/6/91	74	NA	NA	NA	NA
4/7/91	75	NA	1	NA	32.7
4/8/91	76	78.2	1	NA	28
4/9/91	77		1	NA	40.4
4/10/91	78	108	1	NA	20
4/11/91	79	94	1	NA	12

A-11 (cont..)

Date	Days After Startup	NH3-N (I) mg/l	NH3-N (E) mg/l	NO3-N (I) mg/l	NO3-N (E) mg/l
4/12/91	80	96	NA	NA	NA
4/13/91	81	NA	2	NA	NA
4/14/91	82	NA	1	26.8	10.6
4/15/91	83	84	1	24.4	8.9
4/16/91	84	80	1	20.9	6.2
4/17/91	85	75	1	22	5.4
4/18/91	86	75	1	27.5	3
4/19/91	87	76	NA	26	NA
4/20/91	88	NA	NA	NA	NA
4/21/91	89	NA	1	NA	0.95
4/22/91	90	13	1	21.4	1
4/23/91	91	6	1	25.2	1.1
4/24/91	92	5	1	24.5	1.2
4/25/91	93	4	1	23.1	1.2
4/26/91	94	6	NA	25.6	NA
4/27/91	95	NA	NA	NA	NA
4/28/91	96	NA	1	NA	0.7
4/29/91	97	6	1	27	0.7
4/30/91	98	6	1	25.9	0.65
5/1/91	99	6	2	21.4	0.75
5/2/91	100	8	1	24.7	1.6
5/3/91	101	7	NA	25.3	NA
5/4/91	102	NA	1	NA	NA
5/5/91	103	NA	1	NA	NA
5/6/91	104	77	1	22.6	NA
5/7/91	105	85	1	17	1
5/8/91	106	78	NA	26	NA
5/9/91	107	NA	1	NA	NA
5/10/91	108	57	NA	22	NA
5/11/91	109		NA	NA	NA
5/12/91	110	NA	NA	NA	NA
5/13/91	111	NA	1	NA	NA

A-12: Reactor Temporal NG

Time, hr	Aqueous Phase NG Concentration, mg/l	Solid Phase NG Concentration, mg/Kg
0.00	85	NA
0.75	48	NA
1.50	33	NA
2.25	22	NA
3.00	9.0	NA
3.75	NA	NA
4.00	5.0	NA
4.50	5.0	NA
5.00	NA	57.2
6.50	NA	NA
8.00	NA	19.7
10.00	NA	6.8
11.50	NA	5.0
13.00	NA	5.0

NA = Not Analysed

A-13: Influent & Effluent TKN and Temperature

(I = Influent; E = Effluent; NA = Not Analysed)

Date	Days After Startup	Temp (I) ° C	Temp (E) ° C	TKN(I) mg/l	TKN(E) mg/l
1/23/91	1	19	23	138.5	83
1/24/91	2	22	24	108	47
1/25/91	3	15	27	114	NA
1/26/91	4	18	27	NA	NA
1/27/91	5	21	27	NA	13
1/28/91	6	24	26	121	12
1/29/91	7	24	26	120	19
1/30/91	8	23	24	420	18
1/31/91	9	16	25	108	17
2/1/91	10	22	23	98	NA
2/2/91	11	21	23	NA	NA
2/3/91	12	20	22	NA	100
2/4/91	13	20	23	219	114
2/5/91	14	20	23	213	55
2/6/91	15	21	23	226	162
2/7/91	16	18	22	534	128
2/8/91	17	21	23	263	NA
2/9/91	18	10	22	NA	NA
2/10/91	19	11	23	NA	135
2/11/91	20	NA	24	222	139
2/12/91	21	NA	24	222	139
2/13/91	22	14	NA	203	140
2/14/91	23	NA	20	154	137
2/15/91	24	6.5	26	185	NA
2/16/91	25	21	NA	NA	NA
2/17/91	26	18	NA	NA	124
2/18/91	27	NA	23	162	117
2/19/91	28	NA	24	176	105
2/20/91	29	20	23	180	100
2/21/91	30	NA	25	163	85
2/22/91	31	20	25	185	NA
2/23/91	32	19	24	NA	NA
2/24/91	33	19	24	NA	54
2/25/91	34	19	23	205	54
2/26/91	35	16	24	334	50
2/27/91	36	18	25	173	50
2/28/91	37	20	24	152	39
3/1/91	38	21	24	137	NA
3/2/91	39	21	24	NA	NA

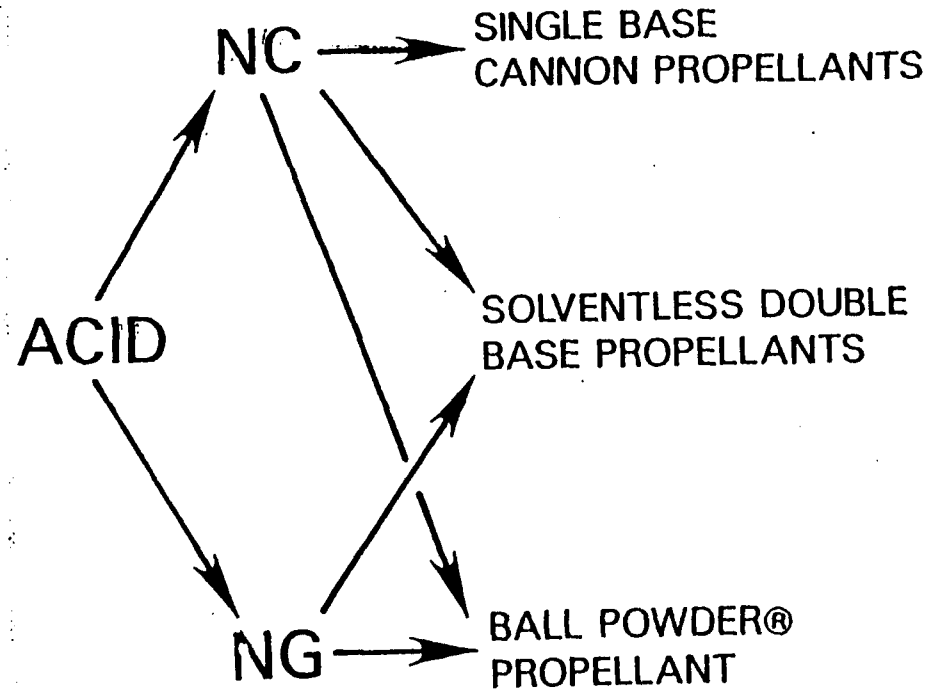
A-13 (cont..)

Date	Days After Startup	Temp (I) ° C	Temp (E) ° C	TKN(I) mg/l	TKN(E) mg/l
3/3/91	40	NA	24	NA	18
3/4/91	41	16	28	185	1
3/5/91	42	9.5	NA	181	4
3/6/91	43	NA	25	172	3
3/7/91	44	17	24	136	5
3/8/91	45	16	24	142	NA
3/9/91	46	NA	25	NA	NA
3/10/91	47	18	25	NA	NA
3/11/91	48	22	26	NA	2
3/12/91	49	22	NA	149	1
3/13/91	50	22	25	155	NA
3/14/91	51	16	25	NA	NA
3/15/91	52	19	24.5	NA	NA
3/16/91	53	19	24.5	NA	NA
3/17/91	54	18	25.5	NA	NA
3/18/91	55	19	25	NA	NA
3/19/91	56	18	25	NA	NA
3/20/91	57	19	27	NA	NA
3/21/91	58	21	27	NA	NA
3/22/91	59	24	27	NA	NA
3/23/91	60	23	27	NA	NA
3/24/91	61	26	25	NA	NA
3/25/91	62	18	25	NA	NA
3/26/91	63	20	25	NA	NA
3/27/91	64	24	25	NA	NA
3/28/91	65	23	24	NA	NA
3/29/91	66	21	25	NA	NA
3/30/91	67	19	25	NA	NA
3/31/91	68	22	26	NA	NA
4/1/91	69	18	26.5	NA	NA
4/2/91	70	19	25.5	NA	NA
4/3/91	71	19	27	NA	NA
4/4/91	72	21	25	NA	NA
4/5/91	73	19	26	NA	NA
4/6/91	74	23	27	NA	NA
4/7/91	75	26	26	NA	NA
4/8/91	76	25	NA	NA	NA
4/9/91	77	NA	22	NA	NA
4/10/91	78	16	24	NA	NA
4/11/91	79	18	24	NA	NA

A-13 (cont..)

Date	Days After Startup	Temp (I) ° C	Temp (E) ° C	TKN(I) mg/l	TKN(E) mg/l
4/12/91	80	19	26	NA	NA
4/13/91	81	19	26	NA	NA
4/14/91	82	20	28	NA	1
4/15/91	83	22	28	34	1
4/16/91	84	21	27	33	3
4/17/91	85	25	27	66	NA
4/18/91	86	22	26	NA	3
4/19/91	87	19	27	47	NA
4/20/91	88	20	27	NA	NA
4/21/91	89	16	26	NA	3
4/22/91	90	22	26	67	4
4/23/91	91	21	26	57	3
4/24/91	92	20	27	58	NA
4/25/91	93	23	25	NA	3
4/26/91	94	19	26	58	NA
4/27/91	95	20	26	NA	NA
4/28/91	96	19	27	NA	5
4/29/91	97	22	27	60	6
4/30/91	98	24	26	62	5
5/1/91	99	21	26	63	7
5/2/91	100	20	24	56	5
5/3/91	101	20	26	54	NA
5/4/91	102	22	26	NA	NA
5/5/91	103	23	26	NA	7
5/6/91	104	20	26	57	6
5/7/91	105	19	26	72	9
5/8/91	106	22	26	84	NA
5/9/91	107	19	27	NA	NA
5/10/91	108	26	29	NA	NA
5/11/91	109	26	29	NA	NA
5/12/91	110	26	29	NA	NA
5/13/91	111	27	28	NA	5

CURRENT PRODUCTION CAPABILITIES



CAPACITIES (MILLION LB/MO.)	
NG	1.6
NC	19.5
SB	16.0
DB	2.8
BP	2.8