The AnoxKaldnes Moving Bed™ Biofilm Reactor (MBBR)

Municipal Leachate & Sanitary Treatment

AnoxKaldnes

- Background MBBR
- Leachate Treatment
    - Older Leachate Case
    - Hazardous Waste Site Case
- Cold-weather Nitrification of Sanitary WW
- Total Nitrogen Removal on Sanitary WW

Anox

Started 1986 in Lund, Sweden as spin-off from Lund University
Today working globally.
Main office in Lund, Sweden

Kaldnes

Started in 1989 to commercialize the MBBR technology developed at the Technical University of Trondheim.
Owned by Anglian Water 1994-2002.
Two offices (Tonsberg, Norway & Providence, Rhode Island)

The Anox/Kaldnes Group

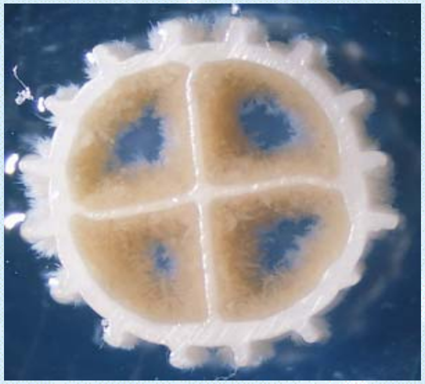
Formed 2003 when Anox acquired 100% of Kaldnes. Now the group is an independent group developing and commercializing new technologies and know-how on the global market.

AnoxKaldnes MBBR

- The process is based on biofilm principles using polyethylene carrier elements.
- The carrier elements, which are less dense than water, provide a large protected surface for bacteria culture.
- MBBR has advantages of AS and TF systems without the disadvantages of those systems.
- The AnoxKaldnes MBBR is the most documented fixed film process with numerous technical publications and presentations.
- Several Process Configurations are available & are based on design requirements: Flow-through MBBR, BAS, & HYBAS

Aerobic MBBR

Anoxic MBBR

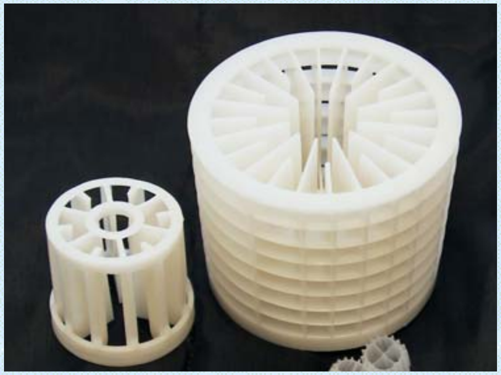


STAINLESS STEEL
RETENTION SCREEN

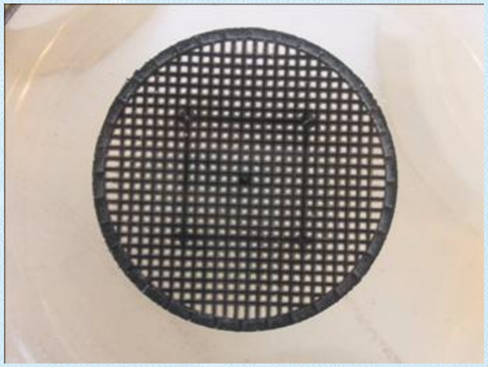
SUBMERSIBLE SLOW-
SPEED MIXERS

Aerobic MBBR

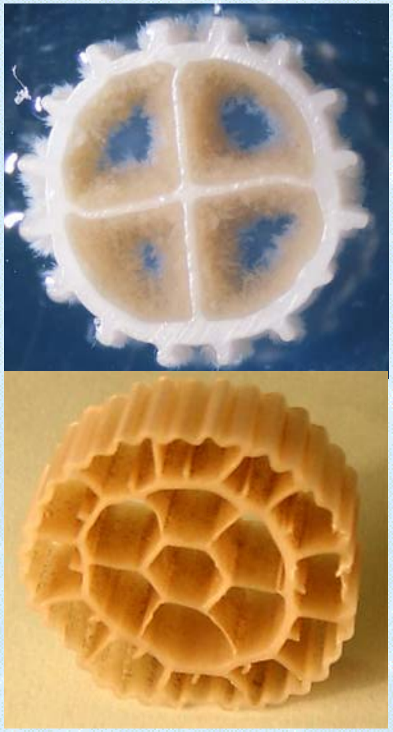
Biofilm Carrier Elements



Natrix® Carriers
Fixed Film Area Varies
P&P or Industrial



BIOFILM CHIP®
1,200 m²/m³ in bulk
366 ft²/ft³
Municipal



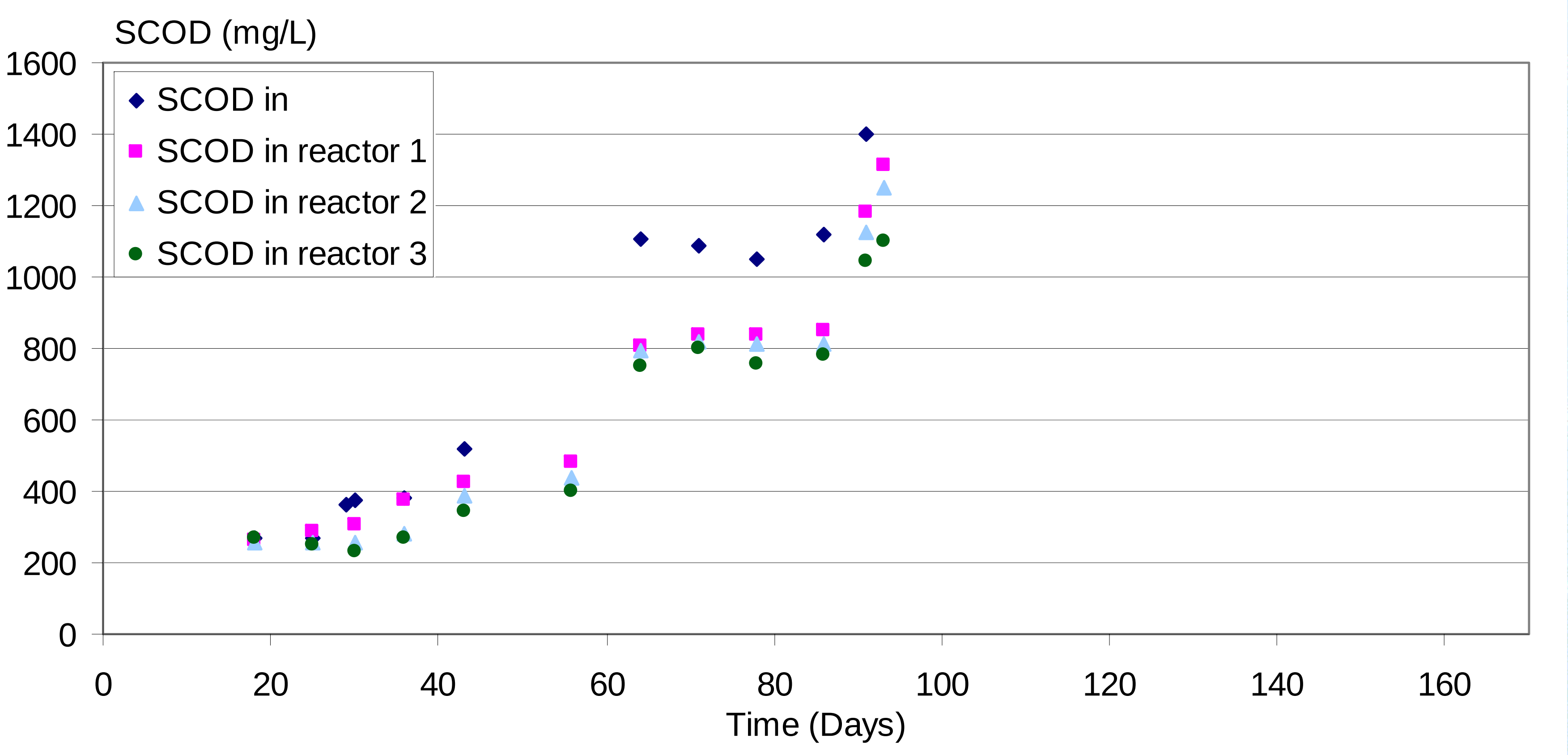
K1 (Top) & K3
500 m²/m³ in bulk
152.4 ft²/ft³
Idustrial / Municipal

LEACHATE TREATMENT - MBBRs

WASTEWATER CHARACTERISTICS

- BOD:COD RATIO – MBBR self adjusts with older leachate
  - Young leachate has BOD:COD ratio with a good amount of degradable organics – assimilation of ammonia is high
  - Older leachate may have high content of recalcitrant organics that are impossible to remove biologically.
  - MBBR biomass would gradually convert from heterotrophic to autotrophic.
- TEMPERATURE ISSUES – not likely with MBBR
  - MBBRs have nitrified at wastewater temperatures < 10C;
  - Lagoon site in Colorado & Quebec nitrified at <3C
- CHEMICAL TOXICITY – not likely with MBBR
  - MBBRs treating 1,4-dioxane – hazardous landfill leachate;
  - MBBRs treating phenols – petrochemical production site;

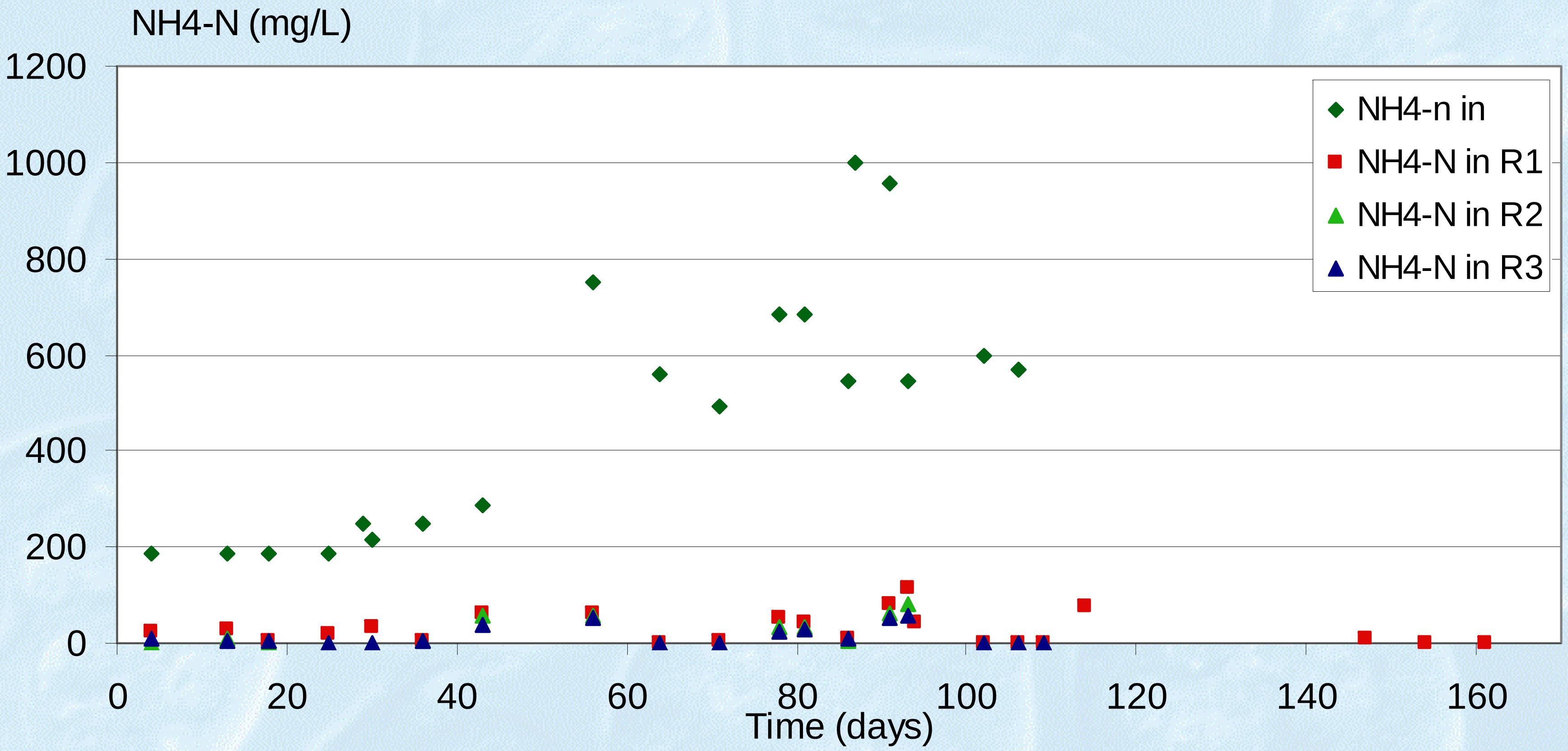
LEACHATE TREATMENT – MBBRs
Mature Leachate



HRT ~1 Day in R1

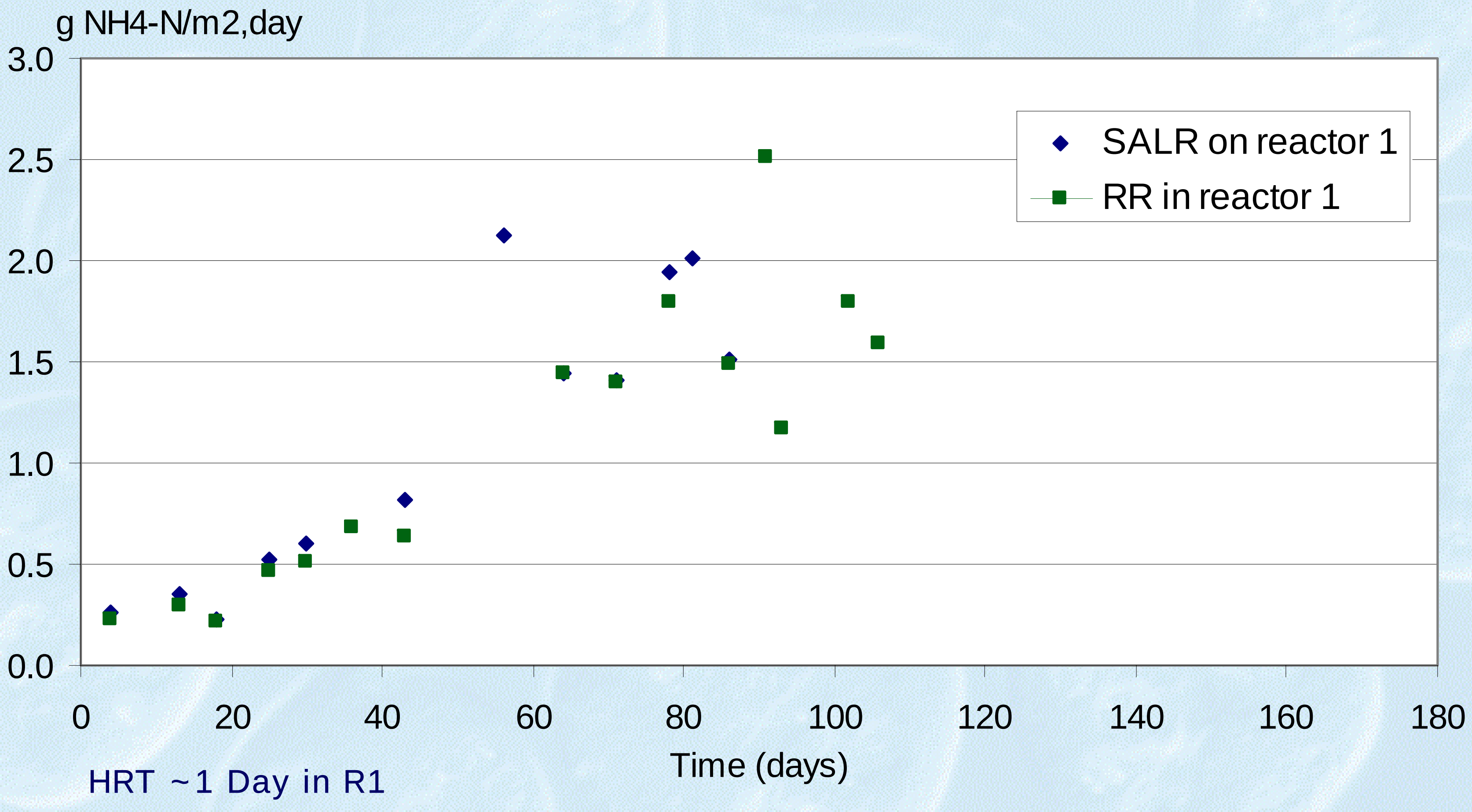
AnoxKaldnes

LEACHATE TREATMENT – MBBRs
Mature Leachate



HRT ~1 Day in R1

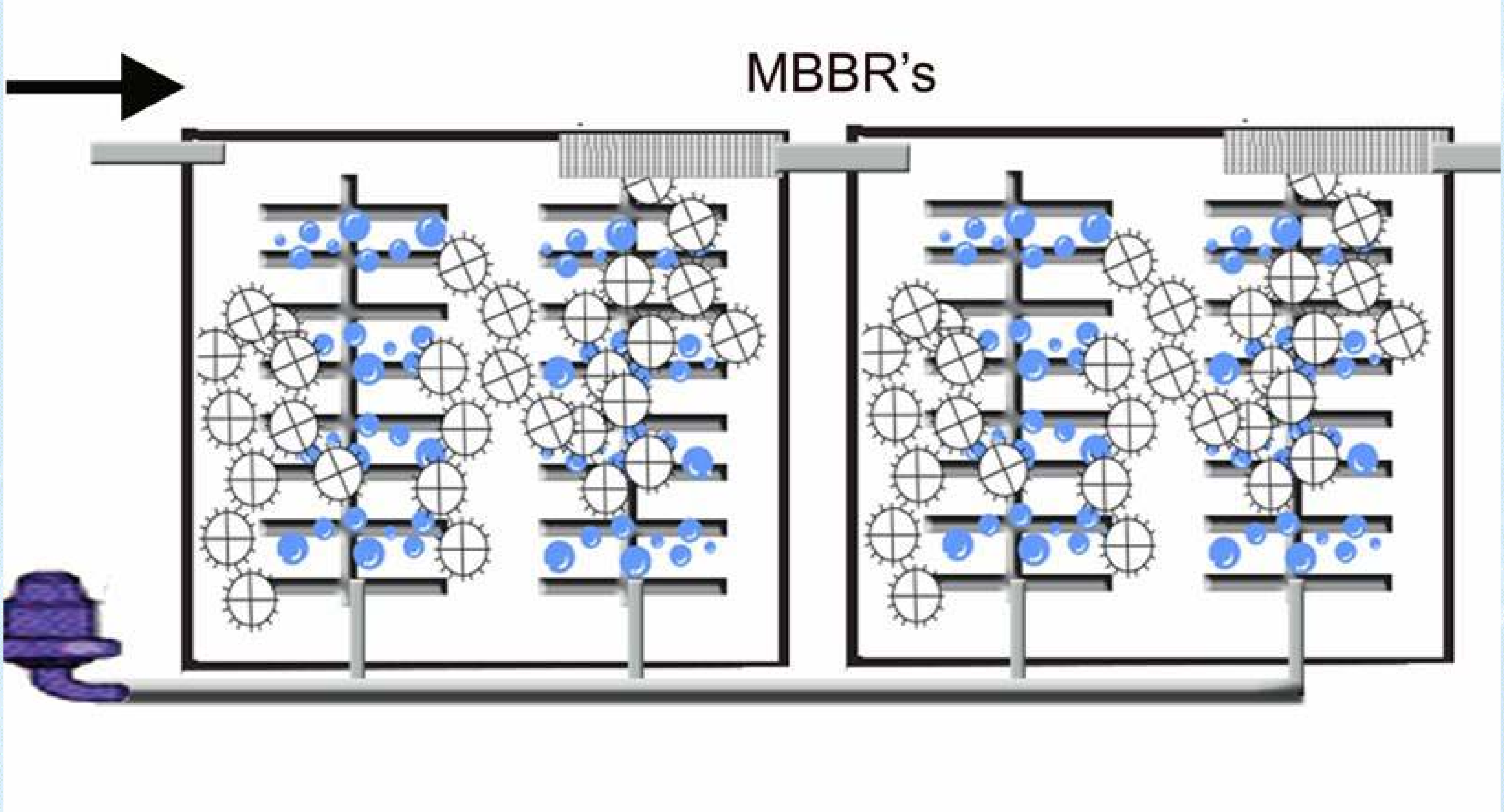
LEACHATE TREATMENT – MBBRs
Mature Leachate



HRT ~1 Day in R1

CASE HISTORY
1,4-dioxane
Removal Using MBBR

Lowry Landfill WWTP



Lowry Landfill WWTP

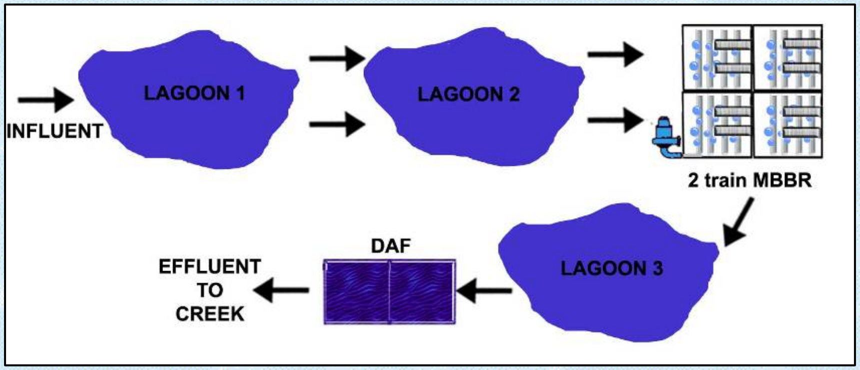
Parameter	Feed to MBBR	MBBR Effluent
Flow	4 m³/day	
1,4-Dioxane	6,400 – 12,000 µg/L	57-83 µg/L
Tetrahydrafuran (THF)	13,500 – 25,000 µg/L	46-212 µg/L
Soluble COD	150-230 mg/L	124-143 mg/L
TOC	62-92 mg/L	52-61 mg/L
TDS	4,300 – 5,000 mg/L	
Ammonia	80-160 mg/L	32 mg/L
Nitrite	0.1-3 mg/L	0.02 – 0.38 mg/L
Nitrite & Nitrate	10-19 mg/L	33-67 mg/L

Lowry Landfill WWTP

- 1,4 – Dioxane degradation >95%
- Reduction in Temperature to 15C – no impact on effluent quality
- In order to nitrify – alkalinity required

CASE HISTORY
Cold Water Nitrification
with MBBR

Johnstown, Colorado



- New NH_3-N Effluent Limits could not be met by Existing Lagoons
- Solution - Retrofit small portion of 3rd Lagoon to MBBR
- Installed 2 process trains of 2 aerobic MBBRs in series
- Installed with 26% fill of Biofilm Carrier Elements to accommodate 0.75 MGD (2,850 m^3/day)
- Can upgrade to 1.5 MGD (5,700 m^3/day) by simply adding media

Johnstown, Colorado

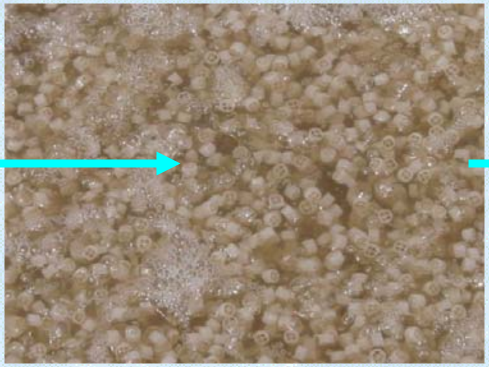
Construction:

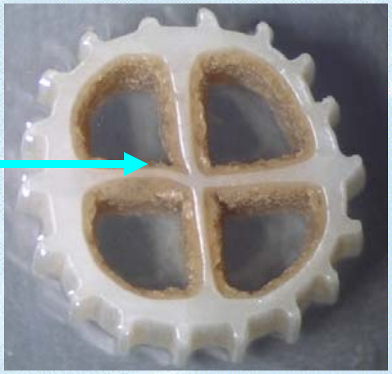
- New concrete basins in area of Lagoon 3
- Total MBBR volume = 1,225 m^3
- HRT = 10.32 hrs Phase 1 Flow
- HRT = 5.16 hrs Phase 2 Flow

Johnstown MBBR

SYSTEM COMPONENTS:

- Biofilm Carrier Elements
- Engineered Aeration System
- Carrier Element Retention Sieves





Johnstown, Colorado

Startup:

- AnoxKaldnes Aeration Pattern
- AnoxKaldnes Retention Sieves
- Algae from Lagoon

Johnstown, Colorado

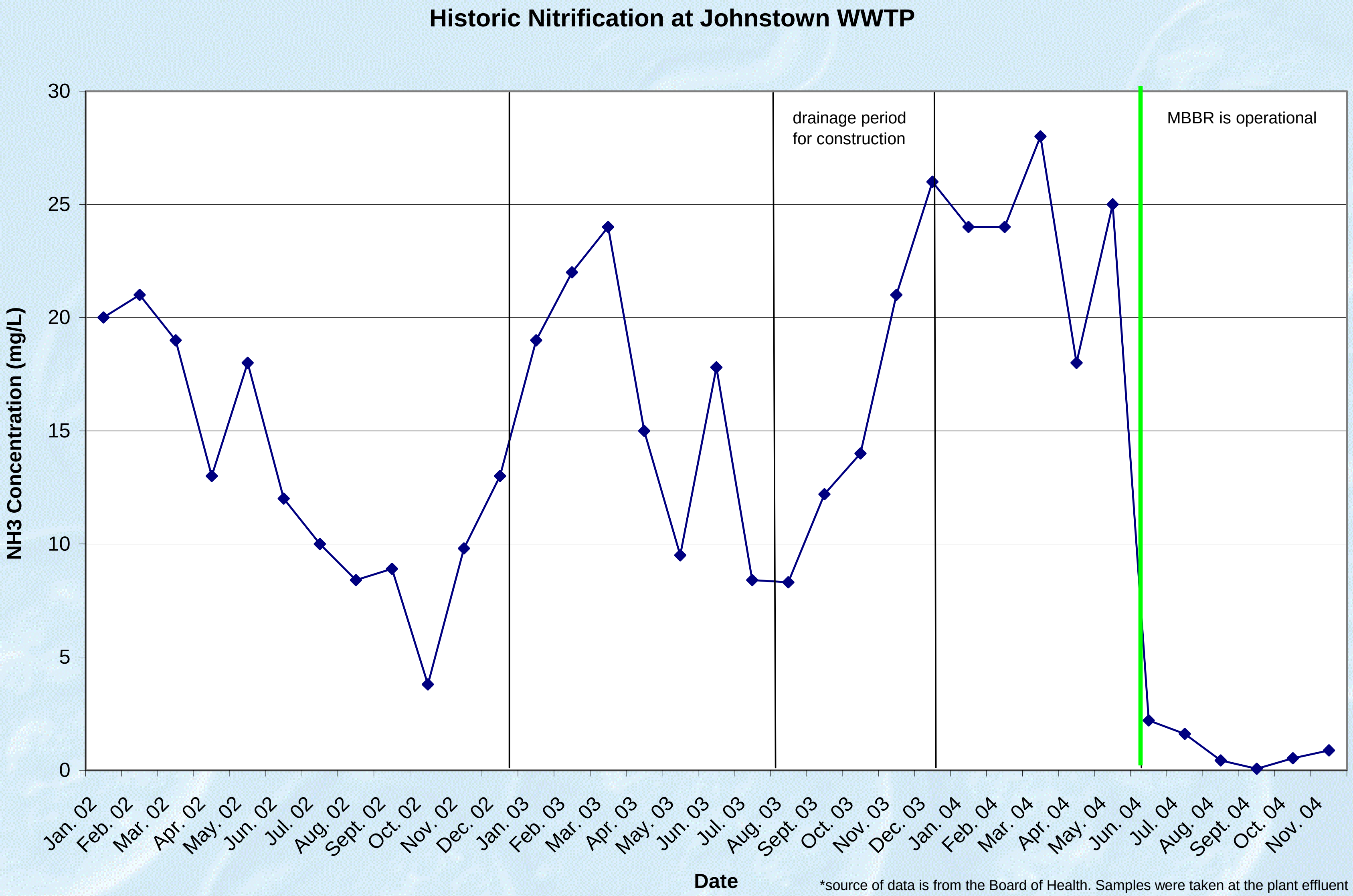
Startup:

- Media Addition
- Fixed Film Assimilation Period 1-4 weeks
- 1 week for organic removal
- 4 weeks for nitrification

Johnstown, Colorado

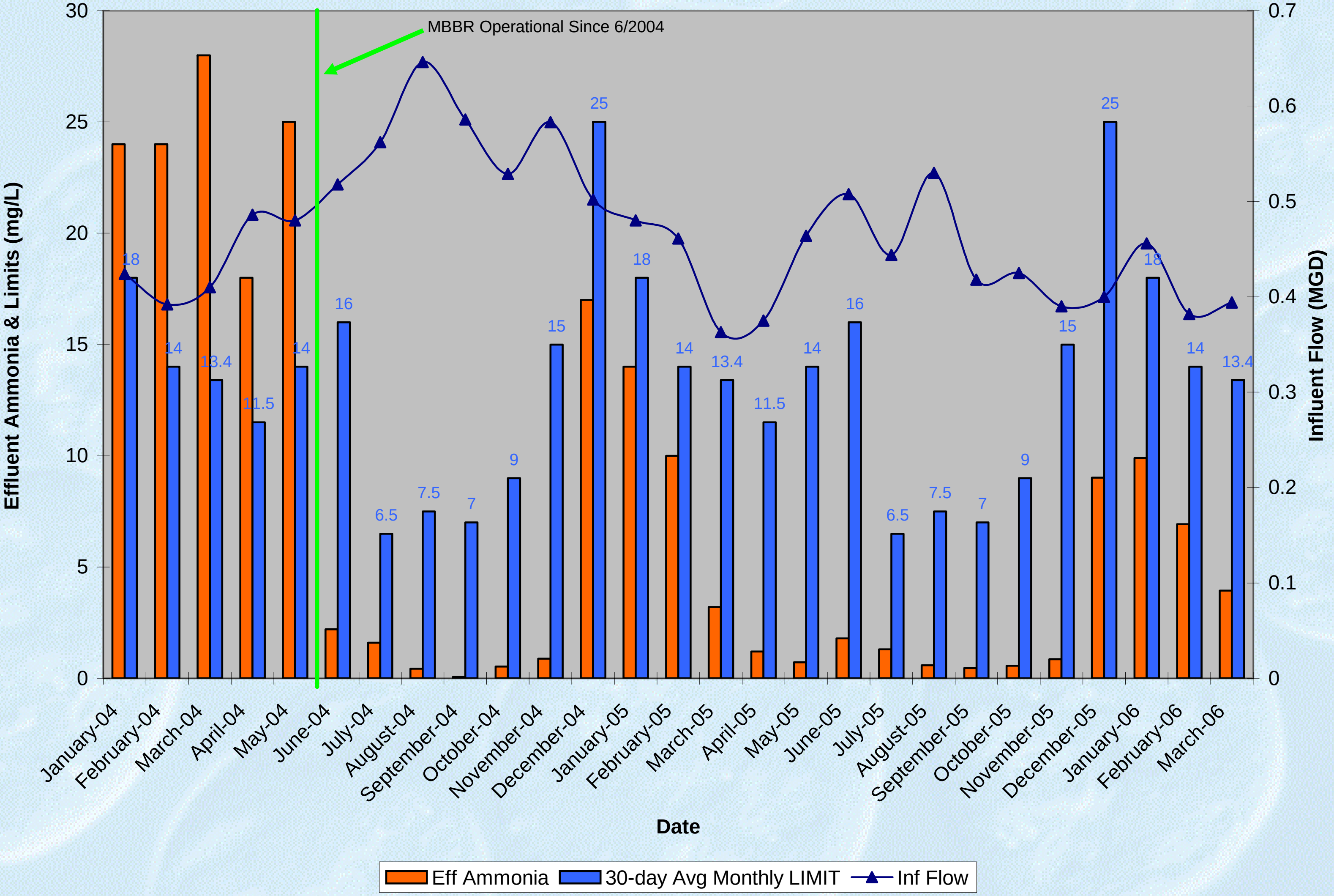
In Operation:

- Aeration System Provides Complete Mix & Oxygen Transfer
- No Algae Problems

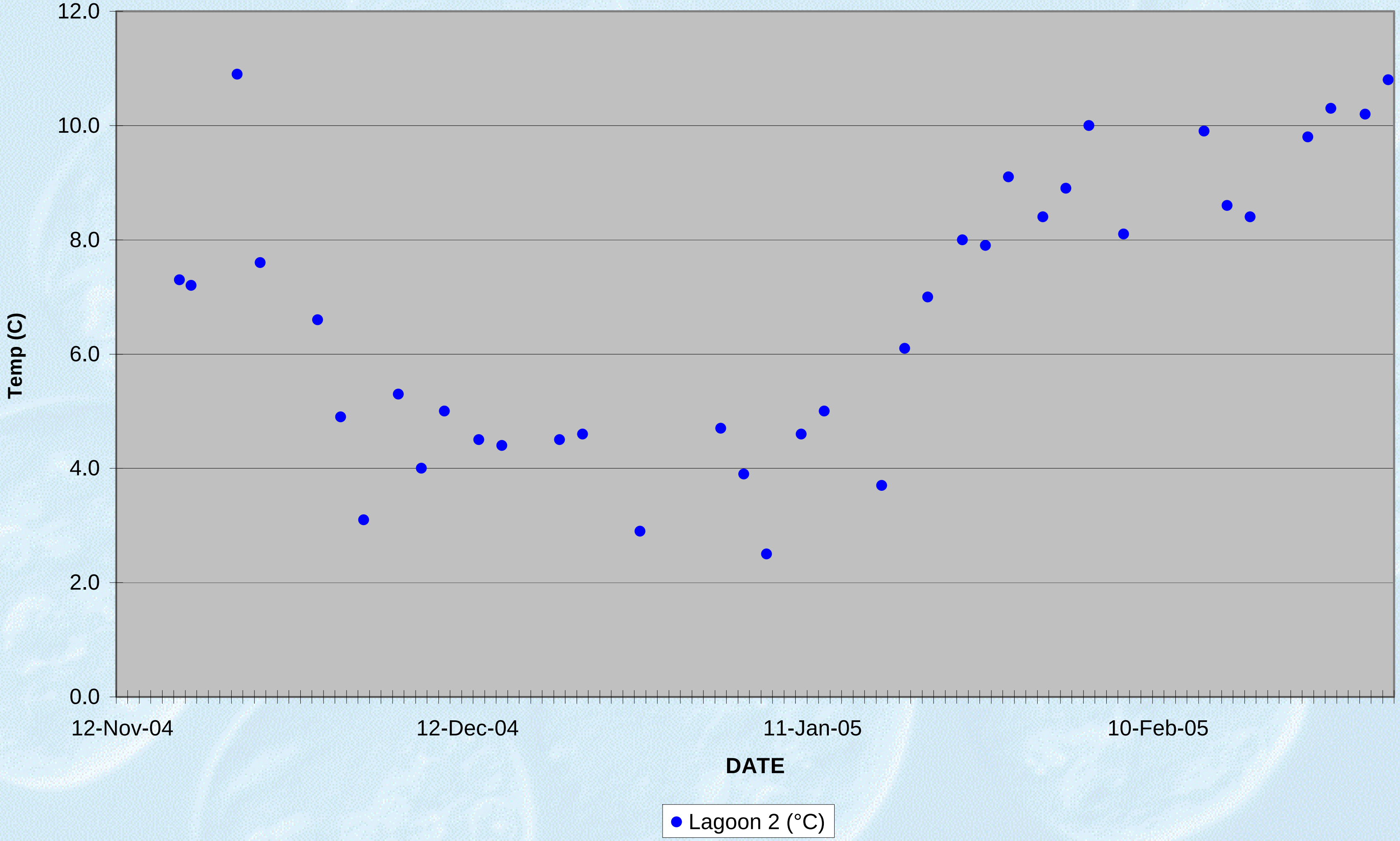


*source of data is from the Board of Health. Samples were taken at the plant effluent pipe at the beginning of each month

Johnstown, Colorado



Johnstown, Colorado



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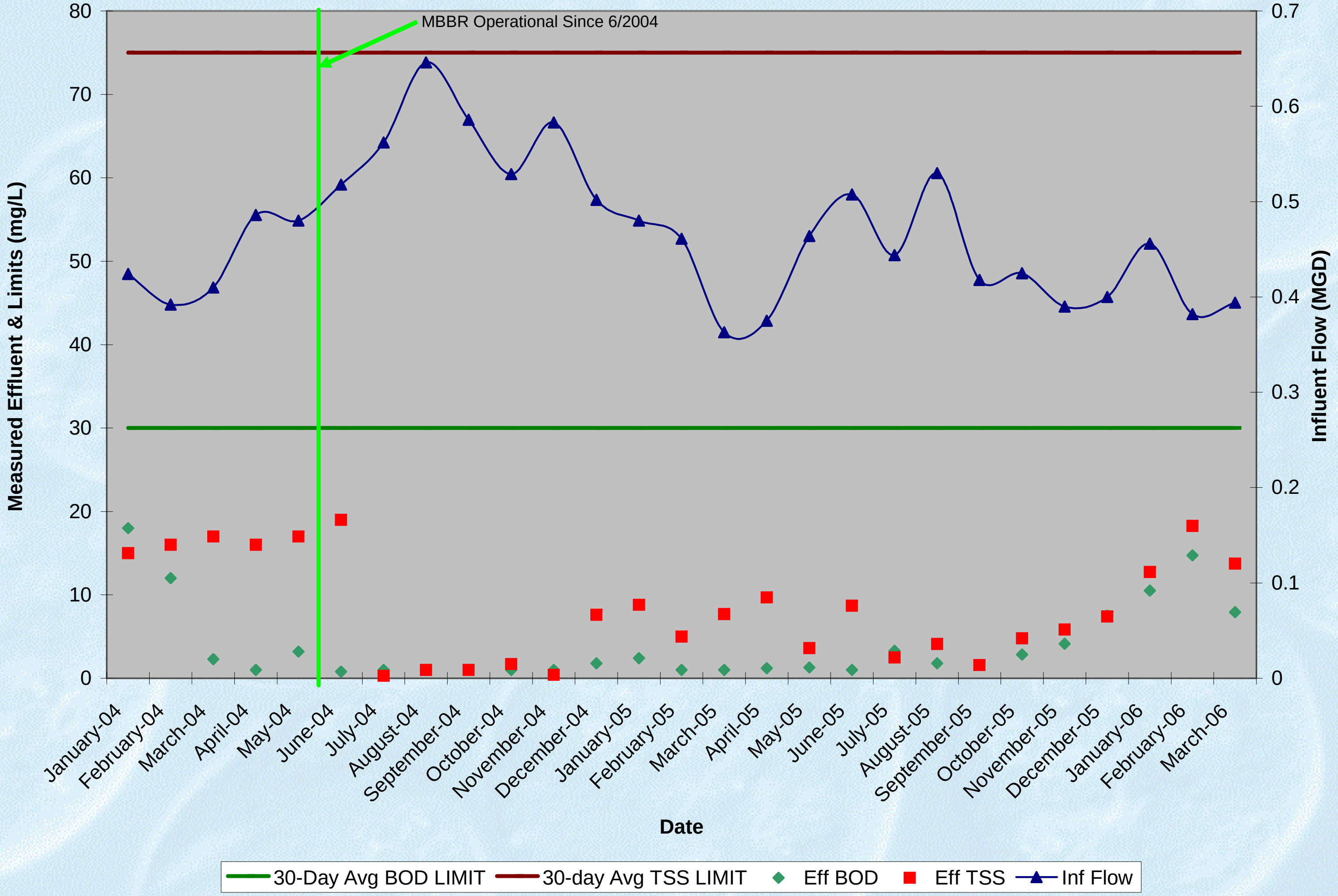
Johnstown, Colorado



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Johnstown, Colorado

Coliform Bacteria Removal

DAF Feed 5,000 CFU/100 ml

DAF Effluent avg. 250 CFU/100 ml

Parameter	DAF Influent		DAF Effluent	
	Range	*Average*	*Range*	*Average*
Turbidity, NTU	18 - 80	40	2 - 28	15
BOD mg/L	24 - 35	27	3 - 13	10
TSS mg/L	19 - 62	35	8 - 25	11

CASE HISTORY
Long-Term TN Removal Using MBBR

Gardermoen WWTP

Gardermoen WWTP Process Hall

Gardermoen WWTP – Inst. 1998

Specific Data on Gardermoen WWTP:

Design Flows:

Dry	5.83 MGD	22,100 m^3/day
Wet	8.24 MGD	31.200 m^3/day

Primary Settling Area

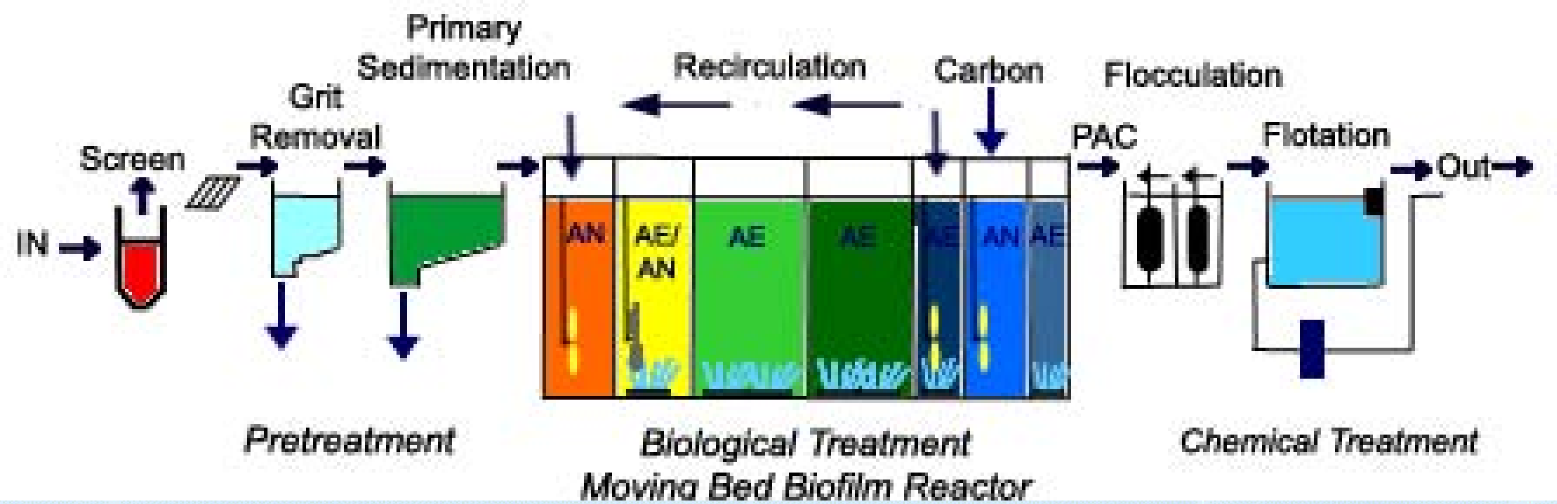
Total Surface Area	4,520 ft^2 (420m^2)
Water Depth	10.8 feet (3.3 m)

Moving Bed Biofilm Reactors

Number of Trains	2
Total Empty Bed Vol.	204,445 ft^3 (5,790m^3)
% fill of Media in MBBRs	42-67%
Water Depth	21.3 feet (6.5 m)

Flocculation Chamber	Total Volume	19,000 gallons
Dissolved Air Flotation	Total Surface Area	2,100 ft^2 (195 m^2)
	Water Depth	8.2 feet (2.5 m)

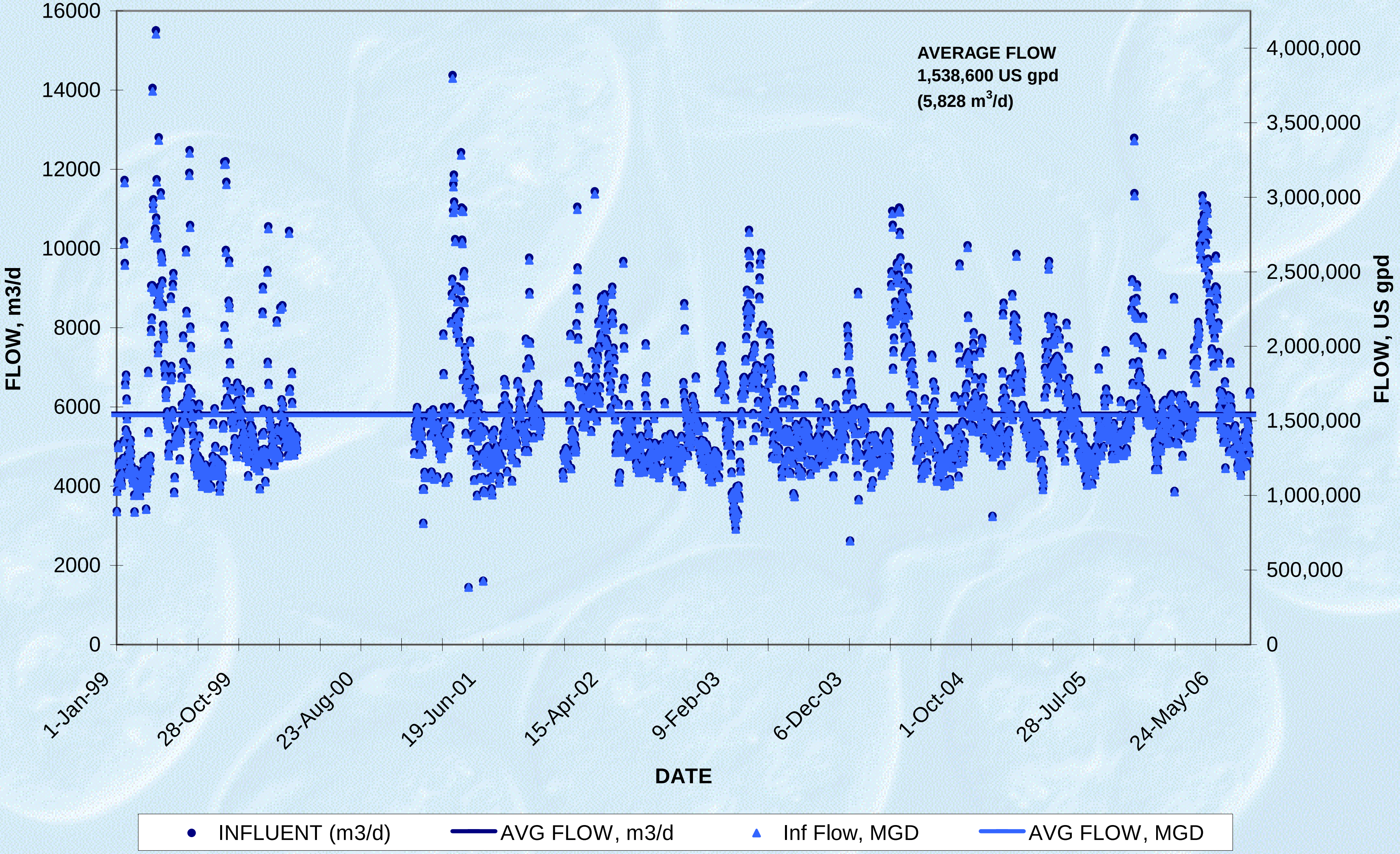
Gardermoen WWTP – Inst. 1998



Specific Data on MBBR

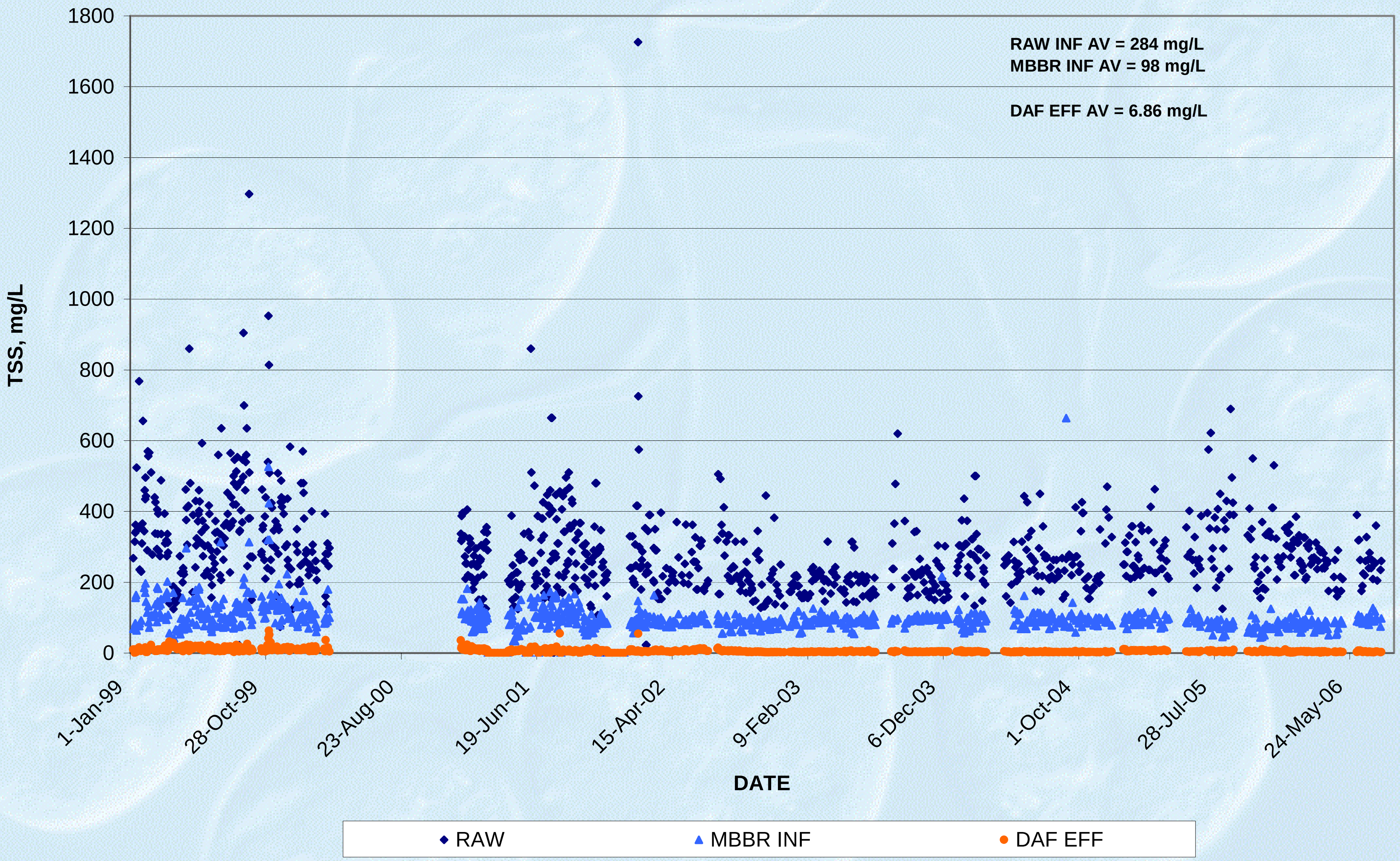
Reactor 1	Volume - 14,830 ft^3 (420 m^3)	Anoxic/Aerobic	67% fill
Reactor 2	Volume - 14,830 ft^3 (420 m^3)	Anoxic/Aerobic	67% fill
Reactor 3	Volume - 24,540 ft^3 (695 m^3)	Aerobic	67 % fill
Reactor 4	Volume - 24,540 ft^3 (695 m^3)	Aerobic	67% fill
Reactor 5	Volume - 6,356 ft^3 (180 m^3)	Anoxic/Aerobic	42% fill
Reactor 6	Volume - 13,241 ft^3 (375 m^3)	Anoxic	67% fill
Reactor 7	Volume - 3,884 ft^3 (110 m^3)	Aerobic	51% fill

GARDERMOEN WWTP

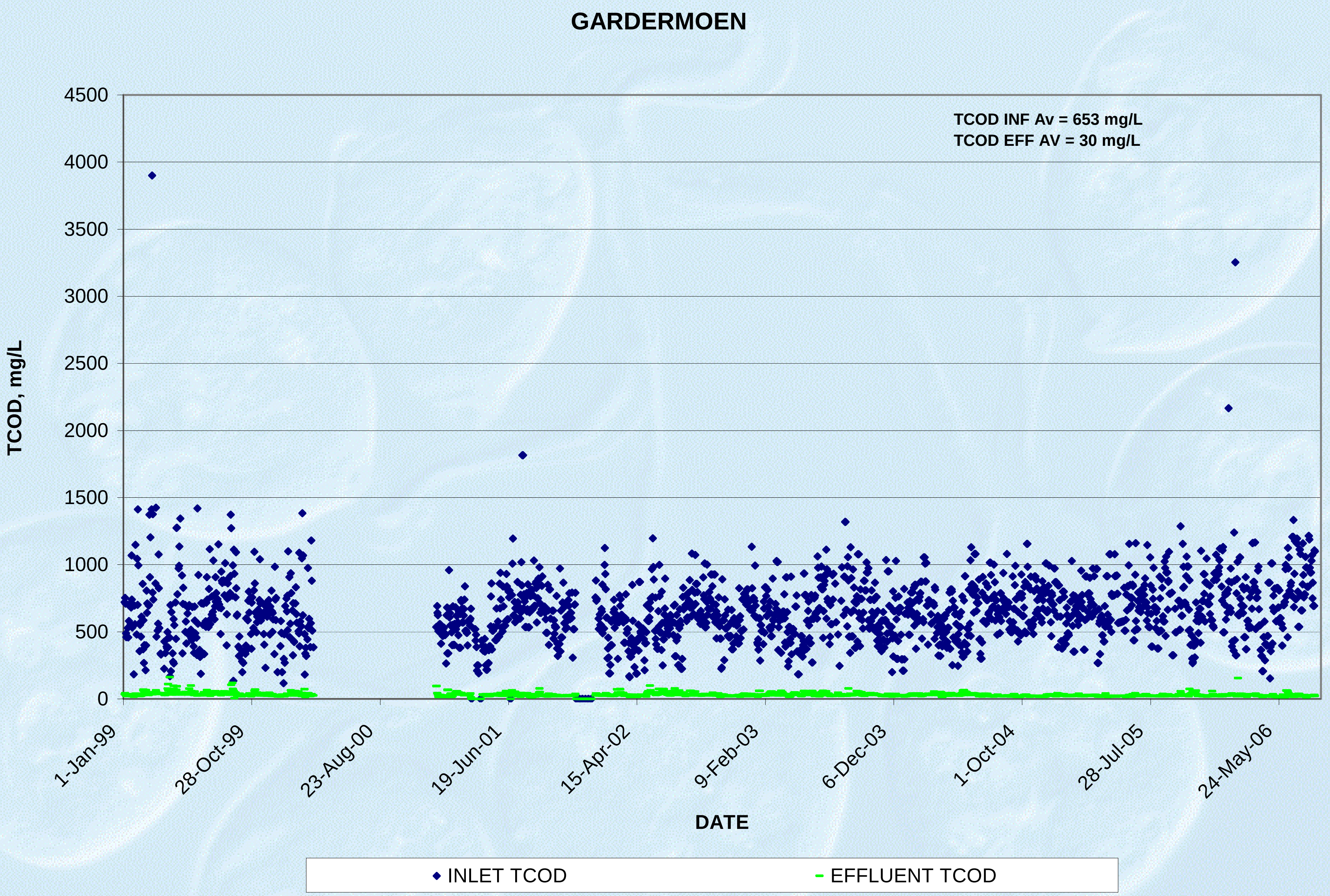


AVERAGE FLOW
1,538,600 US gpd
(5,828 m^3/d)

GARDERMOEN


RAW INF AV = 284 mg/L
MBBR INF AV = 98 mg/L

DAF EFF AV = 6.86 mg/L



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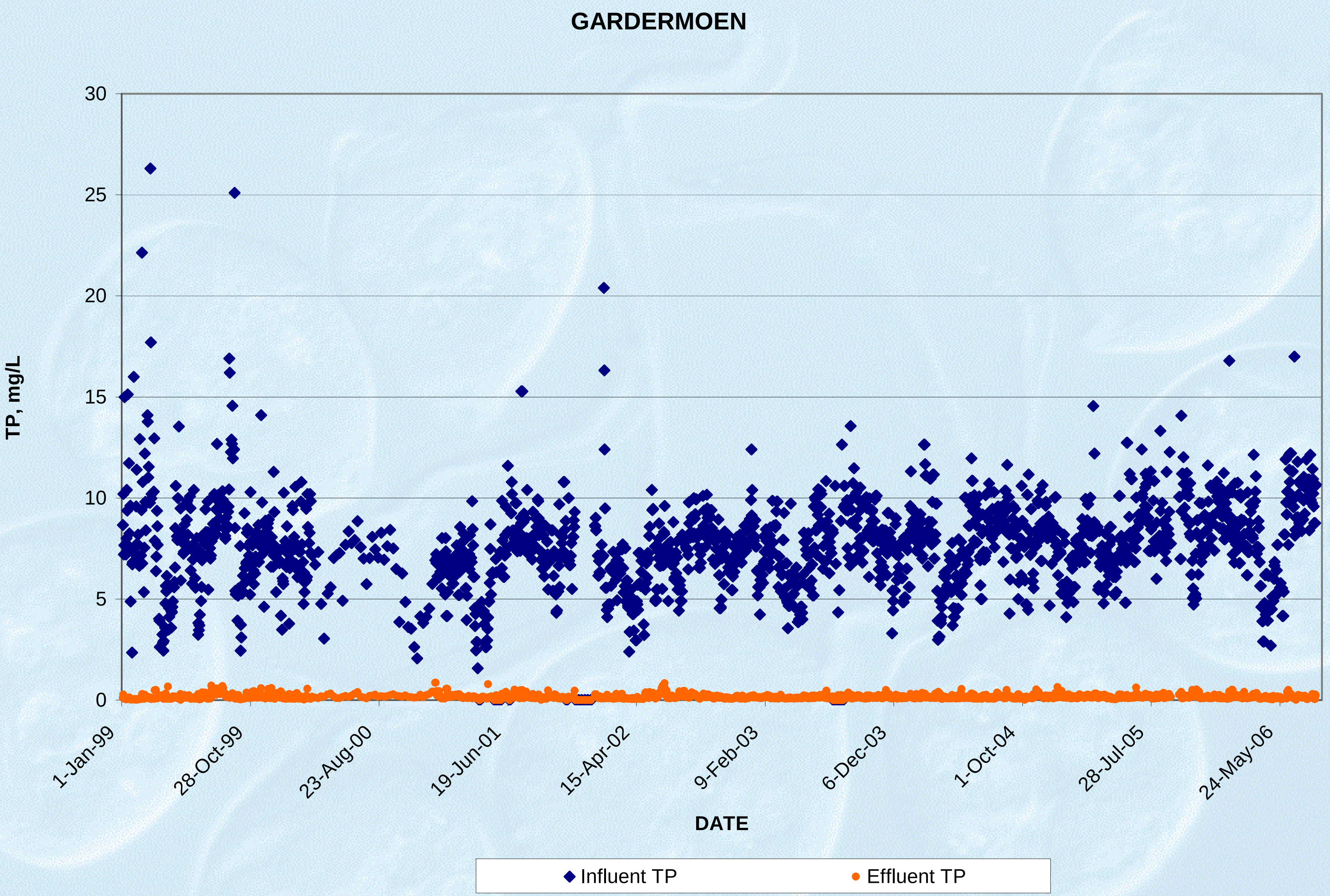
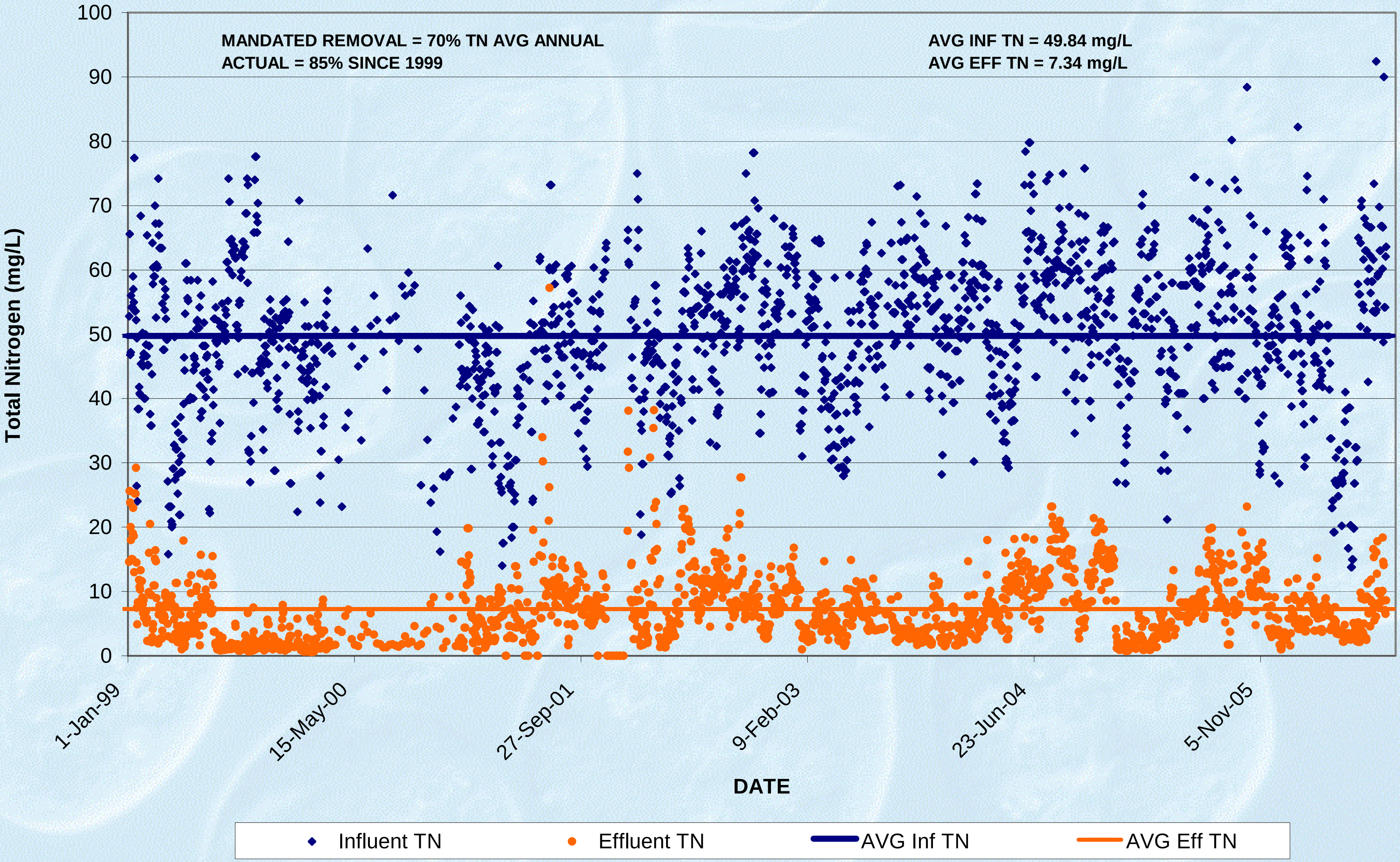
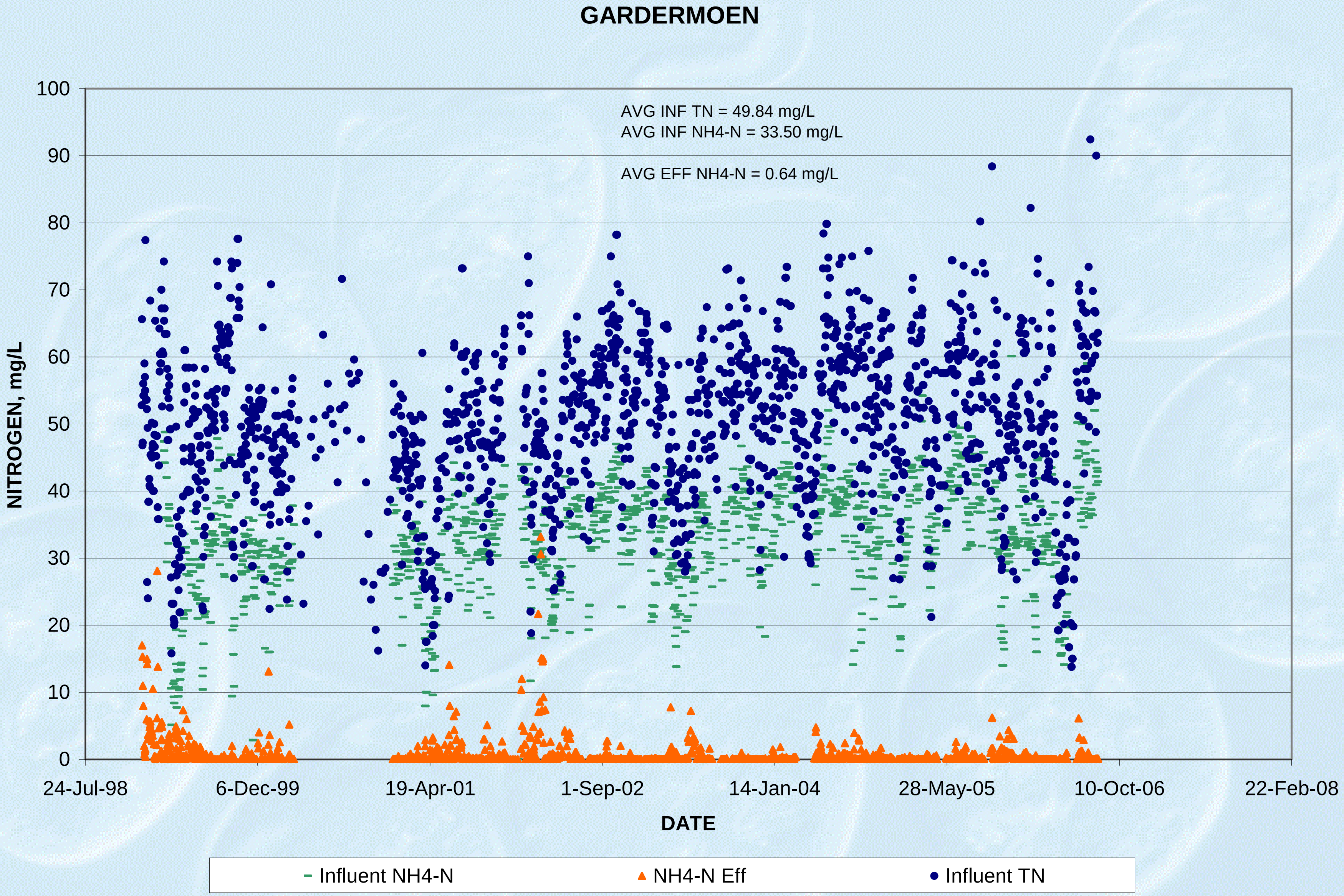

GARDERMOEN
TP, mg/L
30
25
20
15
10
5
0
1-Jan-99
28-Oct-99
23-Aug-00
19-Jun-01
15-Apr-02
9-Feb-03
6-Dec-03
1-Oct-04
28-Jul-05
24-May-06
DATE
◆ Influent TP
● Effluent TP

GARDERMOEN WWTP





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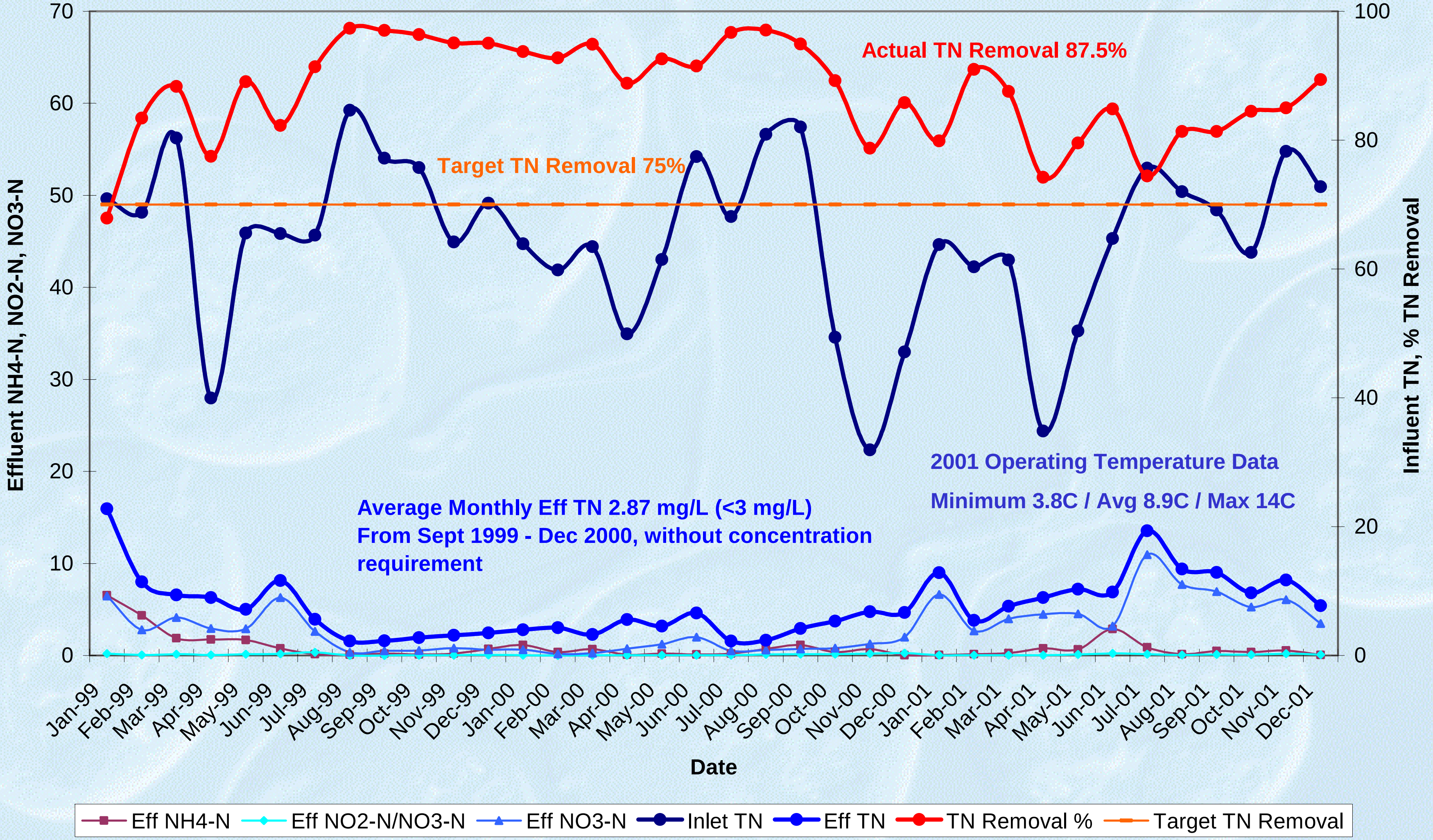
Gardermoen Performance - TN Removal
3-yrs of Data (Monthly Averages)


Actual TN Removal 87.5%

Target TN Removal 75%

2001 Operating Temperature Data

Minimum 3.8C / Avg 8.9C / Max 14C

Average Monthly Eff TN 2.87 mg/L (<3 mg/L)
From Sept 1999 - Dec 2000, without concentration requirement

AnoxKaldnes

Gardermoen WWTP

CONCLUSIONS:

- The use of spent MPG as a carbon source for the MBBR has been a success story at the Gardermoen WWTP. The facility must provide 70% TN removal to remain in compliance.
- Since startup in 1998, the facility has maintained well over 70% TN removal.
- The highest C/N-ratios were only used in order to consume more deicing fluids. At a normal C/N-ratio of 5.5 g COD added/g NO_3-Neq, the effluent NO3-N concentration was sufficiently low and the total N removal of 94 % was more than satisfying.
- At the low C/N-ratio of 2.4 g COD added/g NO_3-Neq, the effluent NO_3-N concentration increased to 8 mg NO_3-N/l. The total N removal efficiency was still 75 %, which shows that the plant may be operated at very low post-denitrification C/N-ratios in order to fulfil the requirement for 70 % total N removal.

PERGAMON

Water Research 37 (2003) 2394–2398

WATER RESEARCH

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Denitrification at low temperatures using a suspended carrier biofilm process

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Received 27 December 2001; accepted 6 January 2003

Abstract

The denitrification process was studied in a stirred lab-scale suspended carrier biofilm reactor at low temperatures (3–20°C). The reactor was filled to 50% with Kaldnes K1 carriers. The denitrification rate showed only a rather weak dependence on the temperature, the rate at 3°C being approximately 55% of that at 15°C. The maximum denitrification rate obtained at 15°C was 2.7 g NO_x^--N m^{-2} carrier d^{-1}. The maximum denitrification rate at 3°C during an 8-day period was found to be constant. During the 8 days, the hydraulic retention time was approximately 1.5 h and the inlet NO_3^--N concentration was 30 mg l^{-1}.

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Keywords: Denitrification; Biofilm; Suspended carrier; Temperature; Psychrotrophic microorganisms

1. Introduction

A problem in dealing with wastewater treatment in the northern part of the world is the low temperature prevailing for most parts of the year since it often is not economically feasible to heat the water, cold-adapted microorganisms are of particular interest for use in microbial treatment processes. The most useful organisms are probably those that are psychrotolerant. These organisms show an optimal growth at temperatures above 20°C, but are still capable of growth at lower temperatures [1]. Psychrotolerant organisms can thus be used over a broader range of temperatures than the psychrophilic organisms, which cease to be active at temperatures above 20°C [1].

A useful application of cold-adapted microorganisms is in the treatment of nitrate-contaminated groundwater through denitrification, since the groundwater in the northern countries is always at a low temperature. Denitrification involves a number of steps in which the nitrate is reduced to nitrogen gas, nitrous oxides (N_2O) or nitrite, depending in particular on the kind of bacteria present and the pH value of the water [2]. Below pH 7, the production of nitrous oxide increases as the pH becomes lower. The pH should be kept above 7, therefore, since nitrous oxide is hazardous both for human health and for the ozone layer [3]. The process should also be optimised with regard to avoiding nitrite accumulation, since nitrite is a toxic compound [4]. The aim of the present study is to investigate the effectiveness of a suspended carrier biofilm process in achieving denitrification at low temperatures (3–20°C).

2. Material and methods

Denitrification was studied in a reactor by use of suspended carriers so as to evaluate the temperature dependence of the process. The double-jacked glass reactor, which had an effective volume of 750 ml, was filled to 50% with the carriers, Fig. 1. The carriers were taken from a denitrification process at a municipal wastewater treatment plant (Malmö, Sweden). The

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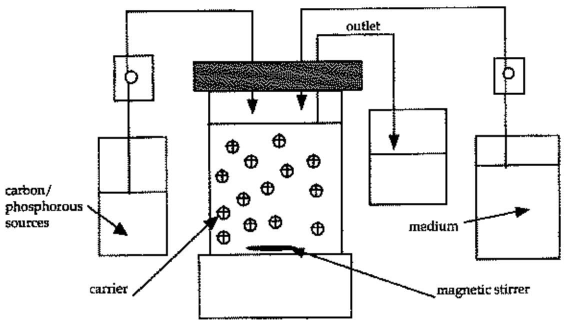

Fig. 1. A schematic presentation of the suspended carrier biofilm process used in the experiments.

average wastewater temperature during the month before the carriers were collected was 9°C. The carriers were kept in suspension with the aid of a magnetic stirrer and were retained in the reactor by use of an outlet pipe smaller in diameter than that of the carriers. The carrier used was Kaldnes K1 (Kaldnes Miljøteknologi, Tønsberg, Norway). The reactor was run at different temperatures (3–20°C) and retention times (0.8–4 h) as shown in Table 1. The temperature was regulated by use of a water bath with a thermostat. After the experiments, the reactor was kept at 3°C and substrate was fed into it for 8 days with a retention time of approximately 1.5 h in order to determine whether the maximum denitrification rate was constant. The medium consisted of 0.182 $\mathrm{g\,l^{-1}}$ $NaNO_3$, 0.0337 $\mathrm{g\,l^{-1}}$ KH_2PO_4 and 0.0382 $\mathrm{g\,l^{-1}}$ NH_4Cl except for when the reactor was kept at 20°C. The medium concentration was then doubled in order to keep the flow rate at a reasonable level, the pump running at maximum speed. A mixture of carbon sources sodium acetate, yeast extract and peptone was added as a separate solution in order to prevent denitrification from already occurring in the inlet vessel. Both the medium and the carbon source solution were kept in a refrigerator. The carbon source solution, for which deionized water was employed, contained 5 $\mathrm{g\,l^{-1}}$ sodium acetate, 3 $\mathrm{g\,l^{-1}}$ yeast extract and 3 $\mathrm{g\,l^{-1}}$ peptone. It was autoclaved at 121°C for 20 min in order to reduce the growth of microorganisms in the inlet vessel. The flow rate was approximately 10% of that in the medium. Tap water was used for the medium in order to ensure that the different trace metals needed were available. In addition, 10 ml of a trace metal solution per litre of medium was added initially so as to facilitate the growth of the biofilm. The trace metal solution contained 2.5 $\mathrm{g\,l^{-1}}$ of $MgSO_4 \cdot 7H_2O$, 1.5 $\mathrm{g\,l^{-1}}$ $CaCl_2 \cdot 2H_2O$, 0.2 $\mathrm{g\,l^{-1}}$ $FeCl_2 \cdot 4H_2O$, 0.55 $\mathrm{g\,l^{-1}}$ $MnCl_2 \cdot 4H_2O$, 0.134 $\mathrm{g\,l^{-1}}$ $ZnSO_4 \cdot 6H_2O$, 0.12 $\mathrm{g\,l^{-1}}$ $CoCl_2 \cdot 6H_2O$, 0.12 $\mathrm{g\,l^{-1}}$ $NiCl \cdot 6H_2O$, 0.085 $\mathrm{g\,l^{-1}}$ $CuCl_2 \cdot 2H_2O$, 6.2×10^{-4} $\mathrm{g\,l^{-1}}$ H_3BO_3, 2.4×10^{-3} $\mathrm{g\,l^{-1}}$ $Na_2SeO_3 \cdot 5H_2O$, 3.3×10^{-3} $\mathrm{g\,l^{-1}}$ $Na_2WO_4 \cdot 2H_2O$ and 2.75 $\mathrm{g\,l^{-1}}$ EDTA triplex III. Addition of the trace metal solution was stopped before the experiment began in order to make the experiment as similar as possible to a real wastewater treatment process. A temperature of 15°C was maintained for 2 weeks prior to the experiment in order to acclimatise the biofilm to the medium. The temperature was kept constant for 1–2 months before it was changed during the experiments. The flow rate was changed at each temperature until the maximum denitrification rate was reached. The maximum denitrification rate was determined when the reactor had been maintained at a constant temperature for at least 1 month in order to make it possible to evaluate the performance of the process after a relatively long time at the same temperature. The idea was to evaluate the process under conditions similar to those, which may be found during cold periods at wastewater treatment plants in countries having a cold climate for at least a part of the year. The pH of both the medium and the carbon source was about 6.7. No pH regulation was performed during the process.

2.1. Batch experiment

A batch experiment was performed to investigate the activity of the organisms when the influence of diffusion was decreased. Collection was made of 100 ml of the effluent, which was poured into an Erlenmeyer flask equipped with baffles. $NaNO_3$ was added to the flask until that the starting concentration became approximately 7 $\mathrm{mg\,l^{-1}}$ NO_3^--N and the air phase was replaced by nitrogen. Nitrogen gas was flushed into the flask from a gas tube for 1 min, after which the flask was sealed by a rubber stopper. A tube for sampling and a needle for gas exchange extended through the stopper. The chemical oxygen demand (COD) and PO_4^{3-}-P concentrations were analysed to ensure that carbon and phosphorous sources were available in sufficient amounts. The flasks were then placed on shaking tables having a rate of 127 rpm. One of the shaking tables was placed in a room at a temperature of 23°C and the other in a cold room at a temperature of 9°C. One flask was placed on each shaking table.

2.2. Analyses

Nitrite and nitrate were analysed according to DIN [5], whereas COD was analysed according to standard methods APHA [6]. Phosphate-P was analysed according to DIN [7]. Total suspended solids (TSS) were analysed as described in the standard methods APHA [6]. The sulphide concentration was determined spectrophotometrically according to the method described in [8]. The oxygen concentration was measured with an Oxi 320 oxygen sensor from Wissenschaftlich-Teschniche-Werkstätten (Hamburg, Germany).

Table 1
Denitrification rate and NO_3^--N, respectively, NO_2^--N concentrations in the reactor operated at different temperatures and HRTs

Temperature (°C)	NO_3^--N (mg l^{-1})	NO_2^--N (mg l^{-1})	HRT	Denitrification rate (g N m^{-2} carrier d^{-1})
20	4.6	0.19	0.92	4.6
20	4.9	0.24	—	4.6
20	4.7	0.25	—	4.6
15	0.4	0.096	3.98	0.7
15	0.4	0.028	1.66	1.4
15	2.8	0.14	0.83	2.7
15	2.8	0.13	—	2.7
15	2.6	0.17	—	2.7
11	0.5	0.017	2.12	1.1
11	1.3	0.024	1.16	1.8
11	1.4	0.026	—	1.8
11	2.0	0.034	0.89	2.5
11	2.4	0.044	0.86	2.6
11	2.4	0.047	—	2.6
11	2.4	0.046	—	2.6
7	0.18	0.013	3.75	0.7
7	2.0	0.14	1.66	1.4
7	2.8	0.20	1.33	1.6
7	2.7	0.20	—	1.6
7	2.7	0.20	—	1.6
3	0.4	0.02	3.61	0.7
3	1.6	0.05	1.66	1.1
3	2.5	0.09	1.41	1.5
3	2.4	0.104	—	1.5
3	2.3	0.100	—	1.5

3. Results

The maximum denitrification rate varied between 1.54 and 4.6 g NO_x^--N m^{-2} carrier d^{-1}, depending on the temperature, as can be seen in Table 1 and Fig. 2. At the maximum denitrification rate, the NO_3^--N concentration in the outlet varied between 2.3 and 4.9 mg l^{-1}, the NO_2^--N concentration remained at around 0.1–0.2 mg l^{-1}. The outlet concentrations were measured three times at the maximum rates in order to determine whether the process was stable. The initial analyses were performed after at least three retention times had passed since this is the minimum time needed for the process to stabilise following a change. The maximum denitrification rate obtained at 3°C was found to be constant during the 8-day period, the NO_3^--N concentration in the outlet remained between 1.7 and 2.5 mg l^{-1} while the NO_2^--N concentration remained between 0.033 and 0.12 mg l^{-1}. The TSS content of the water phase in the reactor was around 0.07 g l^{-1} while the TS content of the biofilm on the carriers was estimated to 5 g l^{-1}. The yield was about 0.3 g TSS per gram of COD removed. Phosphorous and carbon sources were added in excess amounts in order to ensure that neither of these parameters was rate limiting. The PO_4^{3-}-P concentration in the outlet varied between 6 and 8 mg l^{-1}, the COD concentration varied between 300 and 500 mg l^{-1}. The oxygen concentration in the reactor varied between 0.1 and 0.2 mg l^{-1}.

The denitrification rate did not decrease to any greater extent between 15°C and 11°C than between 7°C and 3°C, as can be seen in Fig. 2. The decrease in rate between 15°C and 3°C is relatively small, the rate at 3°C being approximately 55% of that at 15°C. The shape of the curve could be partly a result of the organisms, growing rapidly enough at higher temperatures to prevent their being washed out from the liquid phase. Microscopic examination indicated the outlet to contain higher amounts of free-swimming bacteria when the process was kept at 20°C than when it was kept at either 15°C or 3°C. At all three temperatures the outlet contained relatively large amounts of flocs.

Microscopic inspection of the biofilm after that the reactor had been kept at 3°C for 8 days showed the film to be rather thick and diffuse, which is typical for a denitrifying film. The film also contained small amounts of filament forming bacteria, some of which were able to reduce sulphur. The film also contained a few black crystals as well. A spectrophotometric sulphide analysis, however, showed the sulphide concentration to be below the detection limit of approximately 1 mg l^{-1}. This was to be expected since no sulphur-containing salt was

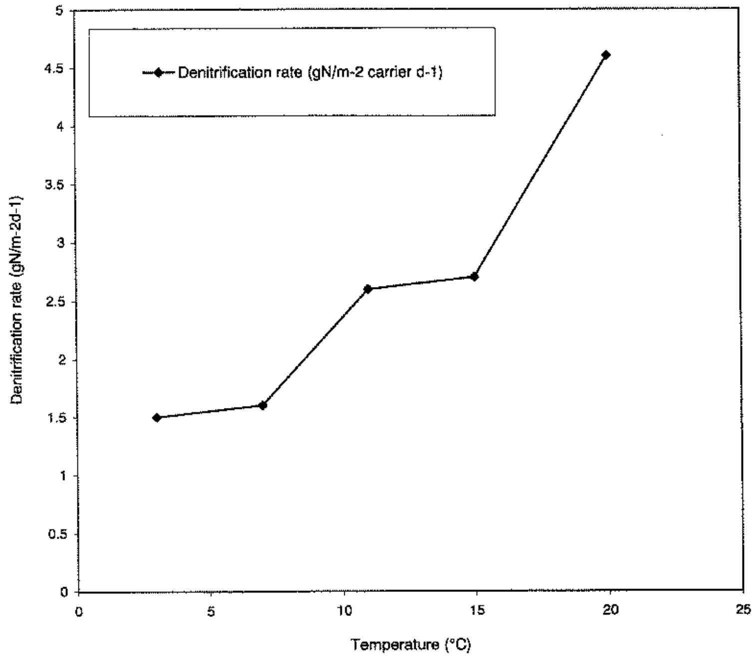

Fig. 2. Maximum denitrification rate as a function of temperature.

added. The sulphur probably came from the yeast extract. The film did not contain any rotifers or ciliates. This was to be expected, since most protozoas and metazoas cannot survive under anoxic conditions. A few flagellates were found in the liquid phase, however.

The batch experiments involving shaking flasks indicated the denitrification rate at 9°C to be approximately a third of that found at 23°C, Fig. 3.

4. Discussion

The results suggest the suspended-carrier biofilm process to be a useful alternative for denitrification at low temperatures, since the denitrification rate showed only a rather weak dependence on the temperature, the rate at 3°C being approximately 55% of that at 15°C.

The rates obtained in the present study can be compared with those obtained in studies performed on suspended-carrier biofilm processes used in treating wastewater of other types. A study performed at a temperature of 17°C on leachate from a municipal landfill, using methanol as a carbon source and employing a different carrier gave a maximum denitrification rate of about 15.7 g NO_x^--N m^{-2} carrier d [9]. A study performed on municipal wastewater, using the same carrier as in the present study, in turn, gave a maximum denitrification rate of 2.2 g NO_x^--N m^{-2} carrier d^{-1} [10]. The major aim of the latter study was to compare a post- and pre-denitrification process and investigate the effect of changes in the amount of external carbon source added to the inlet of the post-denitrification reactors. The differences in the maximum denitrification rates obtained in the different studies involving essentially the same process can perhaps be explained by differences in the composition of the media, such as the carbon sources employed and the amount of carbon source available. The denitrification rate is generally highest with the use of a low molecular weight carbon source [2].

There appear to be at least two different ways of explaining the temperature dependence of the process. The possibility that the cells are psychrotrophic has already been discussed. This would result in definite activity, even at low temperatures. Use of a biofilm configuration may also involve that the cells operating under diffusional restrictions. This could lead to relatively constant denitrification activity, even if the specific denitrification activity of the microorganisms decreased with decreasing temperature. In order to determine the cause of the behaviour clearly found at low temperatures, it is thus necessary to characterize the temperature dependence of those microbes that are not under diffusional constraints.

An aerobic stage is needed as a post-treatment step in order to ensure that the excess of organic compounds used as a carbon source is removed. Phosphate addition should also be optimised. A filtration/sedimentation step would probably be needed as well in order to reduce the amount of suspended matter found in the water that is treated.

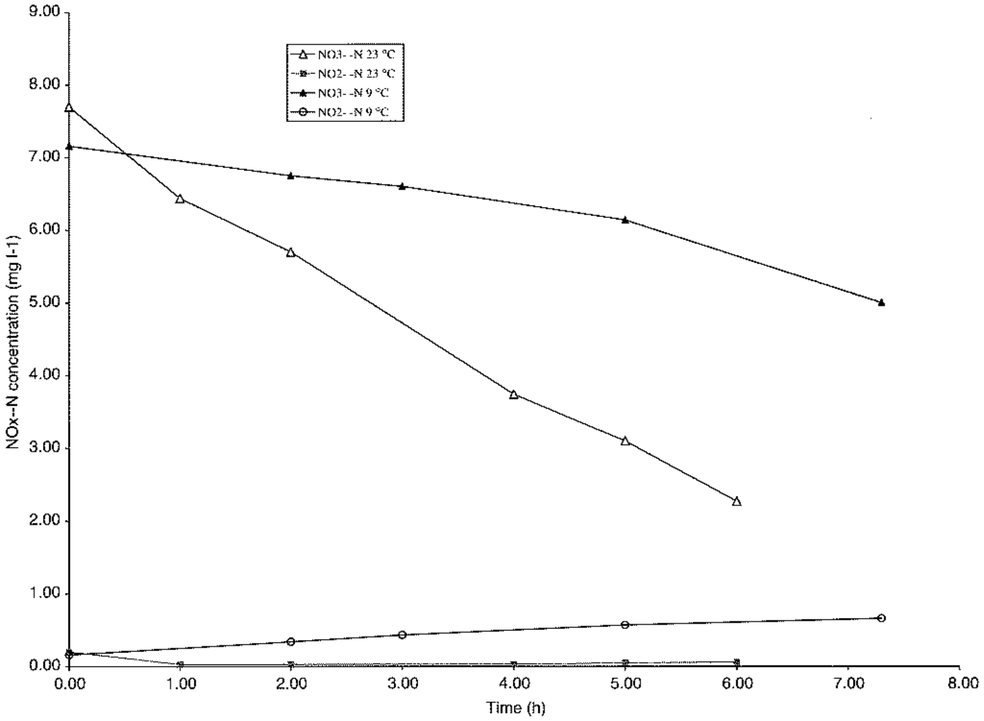

Fig. 3. Concentration of NO_3^--N and NO_2^--N during the batch experiments as a function of time.

5. Conclusions

The relatively weak temperature dependence of the process studied shows it to be of potential use in a cold climate, particularly since the process was shown to be stable, even after relatively long periods of time at a low temperature.

Acknowledgements

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BIOLOGICAL NITROGEN REMOVAL FROM MUNICIPAL LANDFILL LEACHATE IN A PILOT SCALE SUSPENDED CARRIER BIOFILM PROCESS

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Abstract—Leachate from a municipal landfill receiving both household and industrial waste was treated in pilot scale suspended carrier biofilm reactors for removal of nitrogen and organic matter. Nitrification was studied in two parallel aerated reactors, filled to 60% (v/v) with two different models of carrier media with specific surface areas of 210 and 390 m^2/m^3 media, respectively. Denitrification was carried out in a mechanically stirred, anoxic reactor filled to 40% with the carrier media having a surface area of 210 m^2/m^3. Nitrified leachate from one of the aerobic reactors was fed to the anoxic reactor together with external carbon source, initially acetic acid and later methanol, to promote denitrification. The leachate temperature varied between 10 and 26°C during the study. Nitrification proceeded well in this temperature range. The highest volumetric nitrification rate, 24 g N/m^3 reactor h (16°C), was obtained for the media with the largest surface area. The maximum denitrification rate with methanol as carbon source was approximately 55 g N/m^3 h. As the process had reached optimal operation, inorganic nitrogen was almost completely removed and the removal of total nitrogen was approximately 90%. The chemical oxygen demand (COD) removal was around 20% during the study. © 1998 Elsevier Science Ltd. All rights reserved

Key words—nitrification, denitrification, biofilm, suspended carrier, landfill leachate

INTRODUCTION

At many municipal landfills, household waste is deposited together with different kinds of waste of industrial origin, sometimes even hazardous waste. This means that the composition of leachates from municipal landfills might be rather varying depending on differences in the waste deposited. Furthermore, the composition of the leachate from one and the same landfill generally changes considerably with the age of the landfill. In young landfills, containing large amounts of readily biodegradable organic matter, a rapid anaerobic fermentation of this matter takes place, resulting in volatile fatty acids (VFA) as the main fermentation products. This early phase of a landfill's lifetime is called the acidogenic phase, and as much as 95% of the organic content in the leachate can be made up of VFA during this phase (Harmsen, 1983).

As a landfill matures it enters the methanogenic phase. Methanogenic microorganisms develop in the waste, and the VFA are converted to biogas, *i.e.* methane and carbon dioxide. The content of VFA and other readily biodegradable organic compounds in the leachate decreases dramatically and the organic matter in the leachate becomes dominated by refractory compounds, such as fulvic acid-like substances (Harmsen, 1983). In both the acidogenic and the methanogenic phases, most landfill leachates contain high concentrations of nitrogen, mainly in the form of ammonium. The ammonium constitutes an environmental problem as ammonium is toxic in high concentrations (Forgie, 1988) and has fertilizing effects that may lead to eutrophication of the receiving waters.

In order to minimize the negative effects on the environment, landfill leachate must be treated to remove nitrogen and organic compounds before being discharged. At present, a common solution is to treat the leachate together with municipal sewage in the municipal sewage treatment plant. However, this solution has been increasingly questioned due to the concern over the effects of leachates on the biological sewage treatment process and the quality of the sludge generated in this process. It has been indicated that inhibitory compounds in the leachates may disturb the biological sewage treatment process, and the accumulation of hazardous compounds, such as bioaccumulable organics and heavy metals, from the leachates in the sludge formed in the treatment process may make the use of this sludge as fertilizer in agriculture impossible (Lagerkvist, 1986; Linde, 1995).

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As a consequence of the ambition to disconnect landfill leachate from the municipal sewage treatment, the interest in processes for separate treatment of leachate has grown. Methods that have been studied and adopted for use in leachate treatment include suspended growth systems such as aerated lagoons, conventional activated sludge processes and sequencing batch reactors (SBR) (Robinson and Grantham, 1988; Hosomi *et al.*, 1989). As these methods have been found to suffer from different limitations, such as sensitivity to low temperatures and loss of activity due to poor separability of the biomass (EPA, 1975; Knox, 1985), there has been a continued search for other alternatives. A number of investigators have reported on tests on leachate with attached growth systems such as trickling filters (Knox, 1985), submerged aerobic biological filters (Pedersen and Jansen, 1992) and rotating biological contactors (Spengel and Dzombak, 1991). These systems have the advantage of not suffering from loss of active biomass due to poor separability and nitrification in attached growth systems has been shown to be significantly less negatively affected by low temperatures than in suspended growth systems (Knox, 1985).

The suspended carrier biofilm process (SCBP) or moving bed biofilm process is a new type of attached growth system that has gained a lot of interest in recent years (Ødegaard *et al.*, 1994). This process is based on the use of plastic carrier elements which are kept in suspension and movement in the process while the active microorganisms grow as a biofilm on the surfaces of the carrier media. The media is contained in the system by a screen at the outlet of the reactor. The SCBP has become extensively used for nitrification and denitrification of municipal sewage and recently laboratory tests concerning nitrification of landfill leachate in a SCBP have been conducted (Welander *et al.*, 1997). These tests showed nitrification of leachate in this kind of process to proceed at a relatively high rate at temperatures as low as 5°C, indicating this kind of process to be well suited for treatment of landfill leachate under realistic conditions.

The aim of the present investigation was to study biological nitrogen removal from landfill leachate, in a SCBP, on-site at a landfill under realistic conditions (variations in temperature and leachate composition, *etc.*), with the goal of obtaining data that could be used for design of a full-scale process.

MATERIAL AND METHODS

Landfill leachate

Leachate from the Hyllstofta landfill, Sweden, was used in the experiments. The Hyllstofta landfill was started in 1975 and was still in use during the time of this study (1995). The landfill is a traditionally mixed landfill receiving both household wastes and industrial wastes. The industrial waste is dominated by plastic material from a large plastic industry located near the landfill. The total amounts of the different kinds of waste deposited at the landfill at the time of study were 330 000 tons of household waste, 430 000 tons of industrial waste, 190 000 tons of sludge and 100 000 tons of ashes. The amount of leachate produced has typically been between 60 000 and 70 000 m^3 annually. The leachate is collected in a lagoon with a volume of 12 000 m^3 before being discharged to the municipal sewage treatment plant. Leachate from this lagoon was used in the experiments.

The leachate used in the study contained 400–800 mg/l ammonium nitrogen, 800–2000 mg/l COD and a biochemical oxygen demand (BOD_7) of 30–140 mg/l.

Pilot plant trial

The pilot study was carried out in a two-stage suspended carrier biofilm process. The first reactor (reactor 1) was operated aerobically for nitrification and removal of organic matter, while the second reactor (reactor 2) was operated in an anoxic mode for denitrification with addition of external carbon source.

Reactor 1 consisted of a 5 m^3 plastic tank filled to 60% with carrier media (Natrix 6/6C, ANOX AB, Lund). The reactor was aerated by means of a fan and fine bubble membrane diffusers on the bottom of the tank. The pH in the reactor was automatically controlled to 7.0 (day 1–15) and 7.8 (from day 16). Initially, before a significant nitrification was established, the pH adjustment was made with sulfuric acid, while sodium hydroxide was used after a high degree of nitrification was obtained. The reactor was inoculated with 5 m^3 nitrifying activated sludge from the municipal sewage treatment plant in Helsingborg, Sweden, and leachate was fed to the reactor at a flow rate corresponding to a hydraulic retention time (HRT) of 4 days. The HRT was then decreased in stages during the trial to determine the maximum loading capacity of the process.

Reactor 2 was a plastic tank with a volume of 900 l filled to 40% with the same kind of media as reactor 1. The carrier media in reactor 2 was kept in movement by means of a mechanical stirrer (30 rpm). Acetic acid was used as external carbon source from day 1 to 54, after which methanol was used. The dosage of carbon source was adjusted manually during the test with the aim to dose approximately 4 g COD per g NO_3^--N entering the anoxic reactor. Phosphorus in the form of phosphoric acid was dosed to reactor 2 throughout the study in an amount of approximately 10 g phosphorus per m^3 leachate. Reactor 2 was not inoculated except for the inoculum entering the reactor with the effluent from reactor 1 (Fig. 1).

On day 19, a third reactor (reactor 3) was started up in order to compare the performance of a new carrier model with the one used in reactor 1 and 2. Reactor 3 had a volume of 900 l and it was filled to 60% with carrier media (Natrix 12/12C, ANOX AB, Lund). It was operated aerobically for nitrification in parallel with the two-stage system, and without any subsequent denitrification. The reactor was aerated by the same fan as used for reactor 1, but a course bubble aeration system was used. The reactor was inoculated with 900 l of the same activated sludge as used for reactor 1 and the start-up and operating procedures were also the same as for reactor 1 except for beginning at an HRT of 3 days.

Carrier media

Natrix model 6/6C is a plastic carrier made of polyethylene mixed with lime and small amounts of other compounds. Each carrier element is built up of walls (altogether 12) arranged radially to form a cylindrical body with a length and diameter of 32 and 30 mm, respectively. The carrier has an inner surface area of 210 m^2/m^3 carrier. Only the inner surface is available for biofilm growth as the outer surface is continuously cleaned from

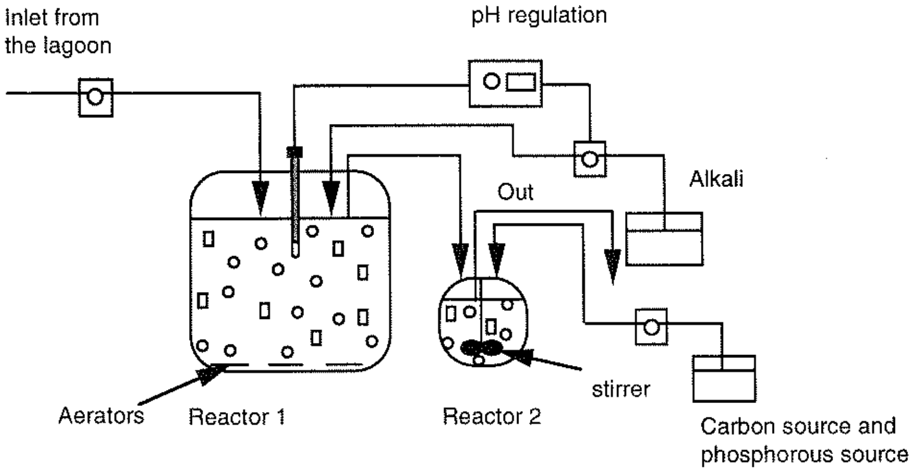

Fig. 1. The experimental setup for reactor 1 and 2.

biofilm by the frequent collisions between the carrier elements. Natrix model 12/12C is similar to model 6/6C except for the number of walls being doubled, resulting in a protected surface area of 390 m^2/m^3 carrier.

Analyses

NH_4^+–N, NO_3^-–N + NO_2^-–N, NO_2^-–N and total nitrogen were measured according to Swedish Standard (SS 02 81 34, SS 02 81 33, SS 02 81 32 and SS 02 81 31, respectively) and COD was analyzed according to Swedish Standard (SS 02 81 42). Total suspended solids (TSS) was analyzed as described in Standard Methods (APHA *et al.*, 1985). BOD_7 was analysed according to Swedish standard SS 02 8193.

RESULTS

The temperature of the leachate varied between a minimum of approximately 10°C and a maximum of close to 26°C during the investigation period (Fig. 2).

Nitrification

During start-up, nitrification increased continuously, resulting in a successively decreasing ammonium concentration in the reactor (Fig. 3). During the first month, nitrite was the main product of nitrification (Fig. 4), but as the ammonium concentration reached a low level, the nitrite concentration dropped dramatically and a complete nitrification to nitrate was obtained (Fig. 4).

The HRT in reactor 1 was kept at 4 days during the first 67 days of the experiment, after which it was decreased to 3 days (Fig. 5). As nitrification was still complete at this HRT, the HRT was further decreased to 2.5 days on day 103. This resulted in a slight increase in the ammonium concentration to a few mg/l, indicating that the maximum capacity of the reactor was reached. The nitrification rate achieved during this period was around 12 g N/m^3 reactor h at a temperature of 17°C.

The biofilm on the carrier media was very thin, barely visible to the naked eye, throughout the test. However, microscopical investigations revealed a compact biofilm containing a large fraction of dense bacterial clusters typical of the growth of nitrifiers. The TSS concentration in both the untreated and the nitrified leachate was approximately 150 mg/l.

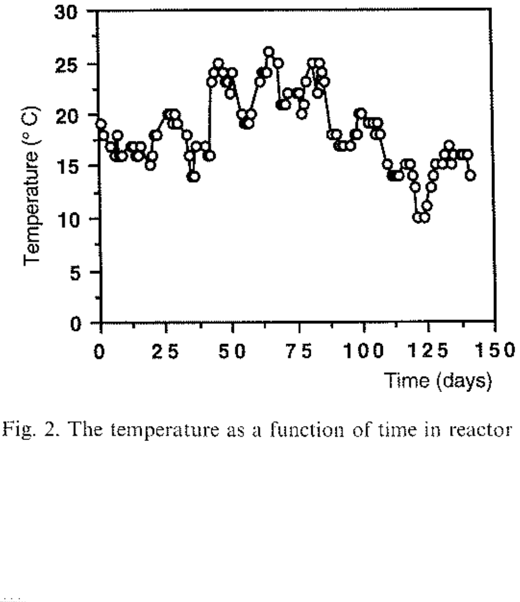

Fig. 2. The temperature as a function of time in reactor 1.

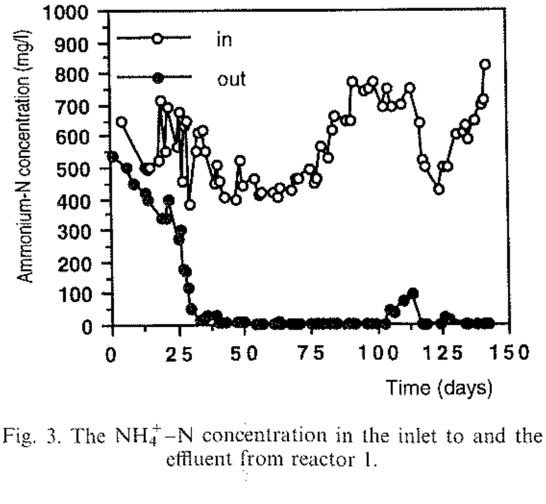

Fig. 3. The NH_4^+–N concentration in the inlet to and the effluent from reactor 1.

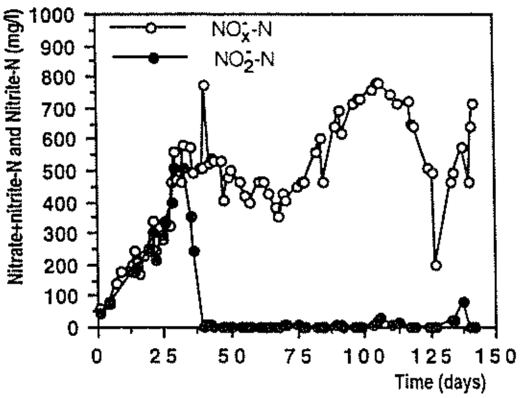

Fig. 4. The NO$_x^-$–N and the NO$_2^-$–N concentrations in the effluent from reactor 1.

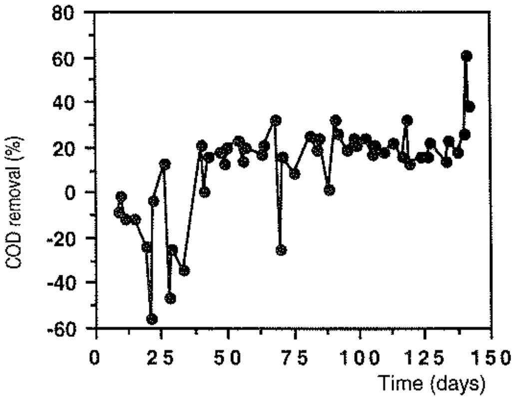

Fig. 6. COD removal in reactor 1 *vs.* time.

Throughout the experiment, the air flow through reactor 1 was regularly adjusted in relation to the loading and the temperature to maintain a dissolved oxygen (DO) level in the reactor between 80 and 90% of the saturation level. On day 112, the HRT was increased to 4.3 days in order to be able to decrease the air flow through the reactor without causing a lack of oxygen. During the final period of the experiment, more air was needed in reactor 3 to be able to test the loading capacity of this reactor and the capacity of the fan was not high enough to supply both reactors with maximum air flows.

During start-up, the COD-level in the leachate increased in reactor 1 (due to nitrite production), after which a COD-removal around 20% was obtained (Fig. 6).

Reactor 3 was started up at an HRT of 3 days (Fig. 5). After approximately two months of operation, a complete nitrification was achieved (Figs 7 and 8). The nitrite production during start-up was considerably lower in this reactor than in reactor 1 (Fig. 8). On day 68, the HRT was decreased to 2.3 days. Initially, a complete nitrification was maintained at this HRT, but as the ammonium concentration in the influent leachate increased, significant levels of ammonium were detected in the reactor (Fig. 7) and a large portion of the ammonium being nitrified ended up as nitrite (Fig. 8). This incomplete nitrification was clearly related to problems keeping the oxygen concentration at a sufficient level during this period; DO levels around 2 mg/l were measured in the reactor. After an increase in aeration on day 100, the DO level increased to around 5 mg/l and both ammonium and nitrite decreased to insignificant levels (Figs 7 and 8). On day 107, the HRT was further decreased to 1.8 days, maintaining a complete nitrification, although significant nitrite levels were measured on a couple of occasions (Figs 7 and 8). On day 118, the HRT was decreased to 1.2 days and the aeration was further increased. At this loading, the ammonium concentration in the reactor increased to a significant level, indicating the maximum capacity of the reactor being reached (Fig. 7). The nitrification rate achieved during this period was around 24 g N/m^3 reactor h at a temperature of 16°C.

The biofilm on the carrier media in reactor 3 had the same character as described above for the biofilm on the media in reactor 1 while the nitrified leachate contained a relatively large number of free living small bacteria and a few flagellates.

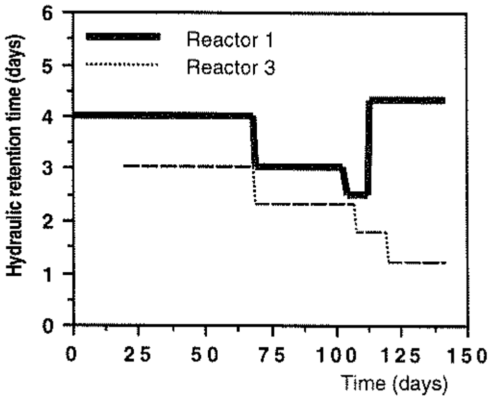

Fig. 5. The hydraulic retention time in reactors 1 and 3 *vs.* time.

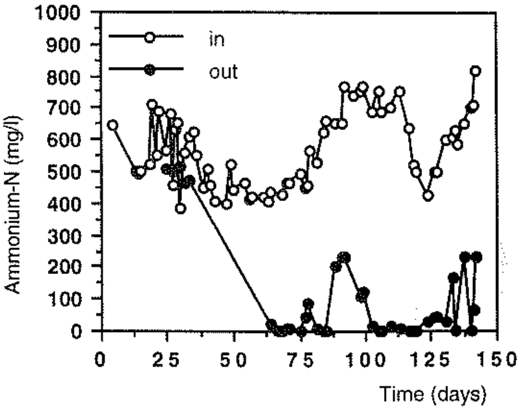

Fig. 7. The NH$_4^+$–N concentration in the inlet to and the effluent from reactor 3.

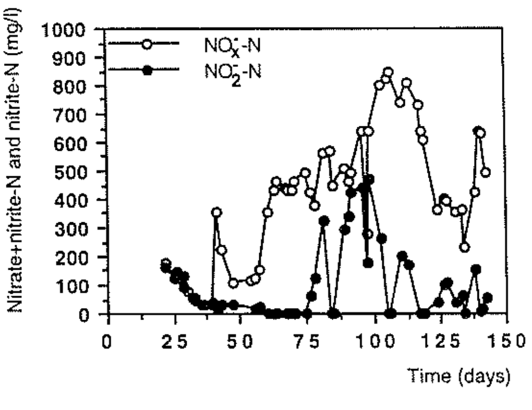

Fig. 8. The NO_x^--N and the NO_2^--N concentrations in the effluent from reactor 3.

Denitrification

As all effluent from reactor 1 was led to reactor 2, the HRT in reactor 2 followed the HRT in reactor 1 throughout the test, being 18% of the later.

Denitrification started quickly as nitrification increased in reactor 1 and nitrate entered reactor 2. After approximately two weeks, a complete denitrification was achieved in reactor 2 at an HRT of 0.72 days (Fig. 9). However, after almost two weeks of complete denitrification, problems balancing the dosage of acetic acid with the consumption led to an overdosage, resulting in a sharp drop in the pH and a severe disturbance of denitrification (Fig. 9). After a period of more careful dosage of carbon source, denitrification recovered. However, to be sure of avoiding another pH-drop, acetic acid was changed for methanol on day 54.

Acclimation of the denitrification process to methanol proceeded rather slowly, the nitrate level decreasing successively during a period of approximately 40 days until a nearly complete denitrification was achieved around day 100. On two occasions during this period, day 82 and day 89, failure of the methanol dosage led to rapid increases in the nitrate level (Fig. 9). On day 103 the HRT in reactor 2 was decreased from 0.54 to 0.45 days, resulting in an increase in the nitrite level up to around 130 mg N/l (Fig. 9). As the HRT was prolonged to 0.77 days on day 112, the nitrate concentration decreased to a low level again. A temporary peak in the concentration occurred around day 134 due to another failure of the methanol dosage. The maximum denitrification rate achieved during the test was around 55 g/m^3 reactor h at a temperature around 17°C. The removal of total nitrogen in the system was approximately 90% when denitrification was close to complete.

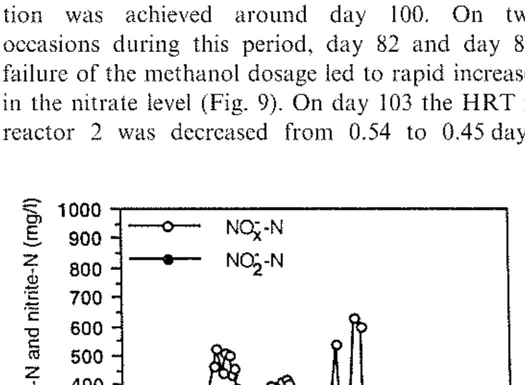

Fig. 9. The NO_x^--N and the NO_2^--N concentrations in the effluent from reactor 2.

During the investigation, a rather thick (0.5–1 mm) biofilm developed on the surface of the carrier media in reactor 2. Microscopical investigations showed a dense biofilm, dominated by rod-formed bacteria. No appendaged bacteria of the *Hyphomicrobium* type, often found in systems denitrifying with methanol as carbon source, could be observed. The liquid phase contained large flocs which settled well and a relatively large number of free living bacteria and low concentrations of flagellates. The TSS concentration was between 300 and 400 mg/l.

DISCUSSION

The results of the present study show suspended carrier biofilm technology to be an interesting alternative for biological removal of nitrogen from landfill leachate. Although denitrification suffered from practical problems with the dosing of external carbon source during a considerable part of the test, the high capacity of the process was clearly demonstrated when the process had acclimated to methanol as carbon source and the dosing worked properly. Under these conditions, a nearly complete removal of inorganic nitrogen and a total nitrogen removal of around 90% were achieved.

The volumetric nitrification and denitrification rates achieved in this study, 24 g N/m^3 h (16°C, reactor 3) and 55 g N/m^3 h (17°C), respectively, were at least as high as the highest rates reported for other types of processes operated on leachate (Table 1).

In the present study, the comparison between the two models of media showed a clear proportionality between the nitrification rate and the surface area of the media. Obviously, the carrier model with the largest surface should be the model of choice for full-scale nitrification of leachate. However, increasing the surface area of the media to an even higher level than 390 m^2/m^3 would hardly further increase the nitrification rate as this would require more narrow flow passages through the carrier elements, decreasing mass transfer. Optimal design of carrier elements for the SCBP always requires a proper balance between media surface area and an openness for free flow to enhance mass transfer, as liquid film diffusion has been shown to be an important parameter in the SCBP (Hem, 1991).

Table 1. The volumetric nitrification and denitrification rates reached by different biological processes operated on leachate and SCBP operated on municipal wastewater respectively leachate

Process	Nitrification rate (g N/m^3 h)	Denitrification rate (g N/m^3 h)	Temperature (°C)	Ref.
Trickling filter	3		16	Knox, 1985
Activated sludge	21		13	Knox, 1985
Submerged aerobic biological filter	24		20	Pedersen and Jansen, 1992
Rotating biological contactor (RBC)	17		20	Spengel and Dzombak, 1991
SCBP, municipal wastewater	12.5–16.7			Rusten *et al.*, 1995a
SCBP, laboratory scale	11–40		20	Welander *et al.*, 1997
Trickling filter		6.3	18–21	Werner and Kayser, 1991
Activated sludge		2.5	18–21	Werner and Kayser, 1991
Fluidized bed		22.9	18–21	Werner and Kayser, 1991
SCBP municipal wastewater		28		Rusten *et al.*, 1995b

The biofilm thickness developed in the anoxic reactor in the tests rules out the use of the media with the largest surface in this application, as the media would most certainly be clogged with biomass. Obviously, different media designs are optimal for different applications of the SCBP. The choice of media has to be based on knowledge of the application and the water to be treated, and factors such as expected biofilm thickness, *etc.*, have to be considered.

The comparison of the reaction rates obtained in the present study with the rates reported for other processes shows that nitrification and denitrification of landfill leachate can be accommodated in a compact process when using suspended carrier technology. Other advantages of the SCBP, as compared to suspended growth systems, such as the activated sludge process, are the simplicity of operation, the low risk of losing the biomass due to poor separability and the weak temperature dependence (Welander *et al.*, 1997). Furthermore, attached growth systems are generally considered less sensitive to toxicity and variations in environmental conditions, a characteristic of value when treating landfill leachate with such a high nitrogen content that there may be risks for substrate as well as product inhibition of nitrification, especially if nitrite accumulates (Anthonisen *et al.*, 1976). The main drawback of the SCBP, and other attached growth systems, is the need for operation at a high DO level to maintain high nitrification rates (Ødegaard *et al.*, 1994). The oxygen dependence of the SCBP has been shown to be approximately first order and not half order as for other biofilm processes (Harremoës, 1982; Hem *et al.*, 1994).

When compared to most other types of attached growth systems, the main advantage of the SCBP is the very good mixing of the reactor contents, resulting in an efficient mass transfer and elimination of the risks of liquid short-circuiting and clogging of the media with biomass or other solids.

The low COD removal achieved in the tests, around 20%, is in agreement with the high COD to BOD ratio of the untreated leachate. The poor biodegradability of the organic content is typical for leachates from landfills in the methanogenic phase, for which most biodegradable organic matter is converted to biogas already in the landfill. The increase in COD over reactor 1 during start-up is explained by the high amount of nitrite formed during this period. As ammonium is not oxidized in the COD analysis, but nitrite is, conversion of ammonium to nitrite in the process results in an increase in COD.

Nitrite accumulation in the aerobic systems occurred mainly during start up and during periods of low DO concentrations (reactor 3) or overloading of the process. Therefore, in a properly designed full scale process, nitrite should not be expected to accumulate except for during start-up. It should also be noted that nitrite accumulation in the aerobic stage is not necessarily a problem, as long as the concentration does not reach a level that is toxic to nitrification. When the aerobic stage is followed by an anoxic stage, nitrite as well as nitrate is removed through denitrification. As a matter of fact, partial nitrification to nitrite followed by denitrification of the latter is an economically favorable process, as less oxygen is needed in the aerobic stage and less carbon source in the anoxic stage than when nitrification goes all the way to nitrate. In view of this, it is more important to avoid nitrite accumulation in the anoxic stage due to partial denitrification (nitrate/nitrite respiration), which could result in discharge of toxic nitrite into the receiving waters. In the pilot plant study, nitrite accumulation in the anoxic stage occurred as this reactor was overloaded. Therefore, when designing a full-scale process, it is important to use a satisfactory safety margin to minimize the risk of nitrite discharge.

The need for process control would be rather limited in a full scale SCBP for leachate treatment. Primarily, the pH in the aerobic stage and the dosing of external carbon source to the anoxic stage would have to be controlled. Even though nitrification is known to have a high optimum pH level, it might be advantageous to start the process at a lower pH, not higher than 7, in order to avoid ammonia toxicity. As nitrification increases, the pH can then be increased to an optimal level, around 7.5, which would also decrease the risk of nitric acid toxicity if nitrite accumulates. This strategy was partly used in the pilot plant trials to be sure of avoiding toxicity problems.

The dosage of external carbon source to the anoxic stage should most certainly be the most tricky parameter to control in a full scale process, especially when the nitrogen content in the leachate shows great variations, as it did during the present investigation. Too low a dose in relation to the nitrate to be denitrified immediately results in decreased nitrogen removal, while an overdosage results in unused carbon source remaining in the treated leachate with increased COD and BOD discharge as a consequence. The latter problem can be avoided by introducing another aerobic stage for removal of any excess carbon source after the anoxic reactor. In practice, this would probably be necessary to avoid BOD discharge. Nevertheless, an efficient dosage strategy is required, as an overdosage followed by aerobic posttreatment is undesirable from an economic point of view. Possibly, carbon source dosage based on on-line nitrate measurements could be an interesting alternative.

CONCLUSIONS

Suspended carrier biofilm technology is an efficient alternative for biological treatment of landfill leachate. A high degree of nitrogen removal can be achieved at high volumetric nitrification and denitrification rates.

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1,4-DIOXANE BIO-DEGRADATION PILOT STUDY AT THE LOWRY LANDFILL SUPERFUND SITE

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ABSTRACT

Groundwater from the Lowry Landfill Superfund Site just outside of Denver, CO, has been treated using a UV catalyzed hydrogen peroxide advanced oxidation process, which has had difficulty removing a target compound (1,4-dioxane) from some Site groundwater streams to low levels due to UV absorbance/interference issues. Bench-scale studies were completed to investigate biological degradation of the target compound. Seven bench-scale conventional activated sludge systems were operated over six months at a variety of feed mixtures, loading rates, and sludge retention times. The bench scale studies showed that 1,4-dioxane is amenable to biological treatment, with removals to below the detection limit at several operating conditions.

Subsequent the bench-scale studies, a Pilot Study was conducted on-site to demonstrate the sustainability of 1,4-dioxane degradation, the consistency of the level of treatment achievable, and to investigate the effects of different operating parameters on the performance of the system. The Pilot Study was operated as a fixed film, moving bed bio-reactor (MBBR) system utilizing Kaldnes® media to support the biological growth. The Pilot Study demonstrated consistent 1,4-dioxane degradation occurred in the presence of tetrahydrafuran (THF) at various operating conditions. Additionally, the study showed that 1,4-dioxane removal efficiency was not significantly affected by temperatures in the 15-25 °C range, at the mass loadings tested.

KEYWORDS:

1,4-dioxane, tetrahydrafuran, landfill leachate, activated sludge, Kaldnes, MBBR

INTRODUCTION

The Lowry Landfill Superfund Site is located approximately 20 miles southeast of downtown Denver, Colorado, in unincorporated Arapahoe County. From the mid-1960s until 1980, the Site was operated as an industrial liquid waste and municipal solid waste landfill. Liquid wastes disposed of at the Site included substances such as industrial liquids and sludges containing chlorinated solvents, heavy metals, and petroleum hydrocarbons.

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As part of the overall remedy for the Site, groundwater is extracted and treated in an on-site water treatment plant (WTP) prior to discharge to the local municipalities wastewater treament facility. The WTP has two primary sources of groundwater, the North Boundary Barrier Wall (NBBW) and the North Toe Extraction System (NTES). The NBBW is a extraction trench used to maintain hydraulic control of groundwater migrating away from the Site and has relatively few organics. The NTES is a trench at the downgradient limit of the landfill and has a high concentration of organics, including 1,4-dioxane and tetrahydrofuran (THF).

The existing groundwater treatment plant consists of (in order of treatment):

- Equalization
- Chemical Softening
- pH Adjustment
- Bag Filtration
- UV/Oxidation
- Activated Carbon

The current treatment is sufficient for most of the permitted parameters, however poor UV transmittance and possible UV interference by inorganics (caused by NTES waters) prevents UV/Oxidation from removing 1,4-dioxane to below the permit limits.

Biological pretreatment was piloted to evaluate whether 1,4-dioxane permit levels could be achieved. Previous bench scale studies indicated that greater than 95% 1,4-dioxane removal efficiencies were possible when feeding a 30% NTES / 70% NBBW Blended water. However, biological reactors fed 100% NTES groundwater showed signs of inhibition, removing just 70% of the 1,4-dioxane. A Pilot Study was performed to further define under what conditions biological treatment was possible, with the four primary objectives of:

1. Evaluating the sustainability and robustness of 1,4-dioxane degradation;
2. Assessing the effect of temperature on the degradation of 1,4-dioxane;
3. Assessing the effect of organic loading on the stability of 1,4-dioxane degradation; and
4. Providing criteria for sizing and design of a full-scale biological treatment system.

Research has shown that both dioxane and tetrahydrofuran (THF) are degradable in fixed film biological systems (Sock, 1993); however, the removal rate was very dependant upon reaction temperature. Sock showed that removal efficiency for dioxane was optimal near 35 °C with activity decreasing at 20 °C. Sock's biomass was developed using a mixture of THF and 1,4-dioxane, but was able to sustain growth with 1,4-dioxane as a sole substrate. Researchers at North Carolina State University (Zenker et al., 2000) developed a culture that could only degrade 1,4-dioxane cometabolically in the presence of THF. Furthermore, Zenker showed that THF acted as a competitive inhibitor of 1,4-dioxane degradation, with the enzymes responsible for the ether degradation preferentially degrading THF, when present.

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MATERIALS AND METHODS

Design and Operation

Two 350 gallon HDPE tanks (PolyProcessing) were used as biological reactors. The reactors were filled to 50% volume with plastic media (specific gravity of 0.98) (Kaldnes®) in suspension to support thebiomass. Once loaded with biomass, the media approached neutral buoyancy and was more easily mixed throughout the reactor. This configuration is a moving bed bio-reactor (MBBR). The media was retained in the reactor by coarse wedgewire screens over the exit piping. The system was initially operated as a sequencing batch reactor (SBR) with the following cycles (times were the base design and were operator adjustable during the study):

1. Fill (120 minutes): Feed was added to the reactors. The fill period consisted of two steps, anoxic fill with just mechnical agitation and an aerated fill. The length of the anoxic fill and aerated fill cycles were determined by the operator based on operational data. Because the feed was added throughout a large portion of the reaction time, the reactor behaved like a continuously stirred tank reactor (CSTR).
2. React (60 minutes): This was the time that the system was allowed to react without feed. The length of the react period depended on the length of the fill period and the kinetics of the biomass. During this time the reactor was mixed and aerated.
3. Settle (30 minutes): This period was a clarification step where mixing and aeration are stopped and the biomass was allowed to settle to the bottom of the reactor and the Kaldnes® media was allowed to float to the top of the reactor.
4. Decant (30 minutes): The clarified effluent was decanted by pump from the reactor to allow volume for additional treatment. The decant time was dependent on the volume of water to be decanted and the flow rate at which it was removed.
5. Idle (0 minutes): The time between the end of the decant cycle and the start of another fill period. The idle time depends on cycling of other reactors in the system and is there to insure that one reactor is filling at all times. No idle time was used during the study.

A piping and instrumentation drawing of the pilot system is provided as Figure 1. Aeration was by fine bubble diffusion (EDI, 2 cfm/each) with the oxygen being provided by facility instrument air. Flow to both reactors was monitored by an inline rotameter and controlled by a needle valve. The cycles noted above were controlled by PLC to allow for the cycling of equipment to meet operational requirements. Both the agitator and the diffusion air were controlled by a PLC operated, normally closed, solenoid valve on the airline from the air receiver.

Temperatures in the reactors were controlled by immersed temperature elements. Both reactors were provided with low-watt-density resistance-type immersible heaters (Chromolox, 12 kW) to allow operation at elevated temperatures (25°C). Reactor 2 was equipped with immersed cooling coils connected to a small external chiller (Aqualogic 22,000 BTU/hr) to allow for simulation of the normal process water temperature (15°C).

Effluent from the tank was pumped from a small section of the tank separated from the media by a wedge-wire screen (Industrial Screen Products). The screen had 5-mm openings to prohibit the media (10-mm diameter) from passing with the effluent. Decant drainage and effluent sampling were performed from this media-isolated portion of the tank.

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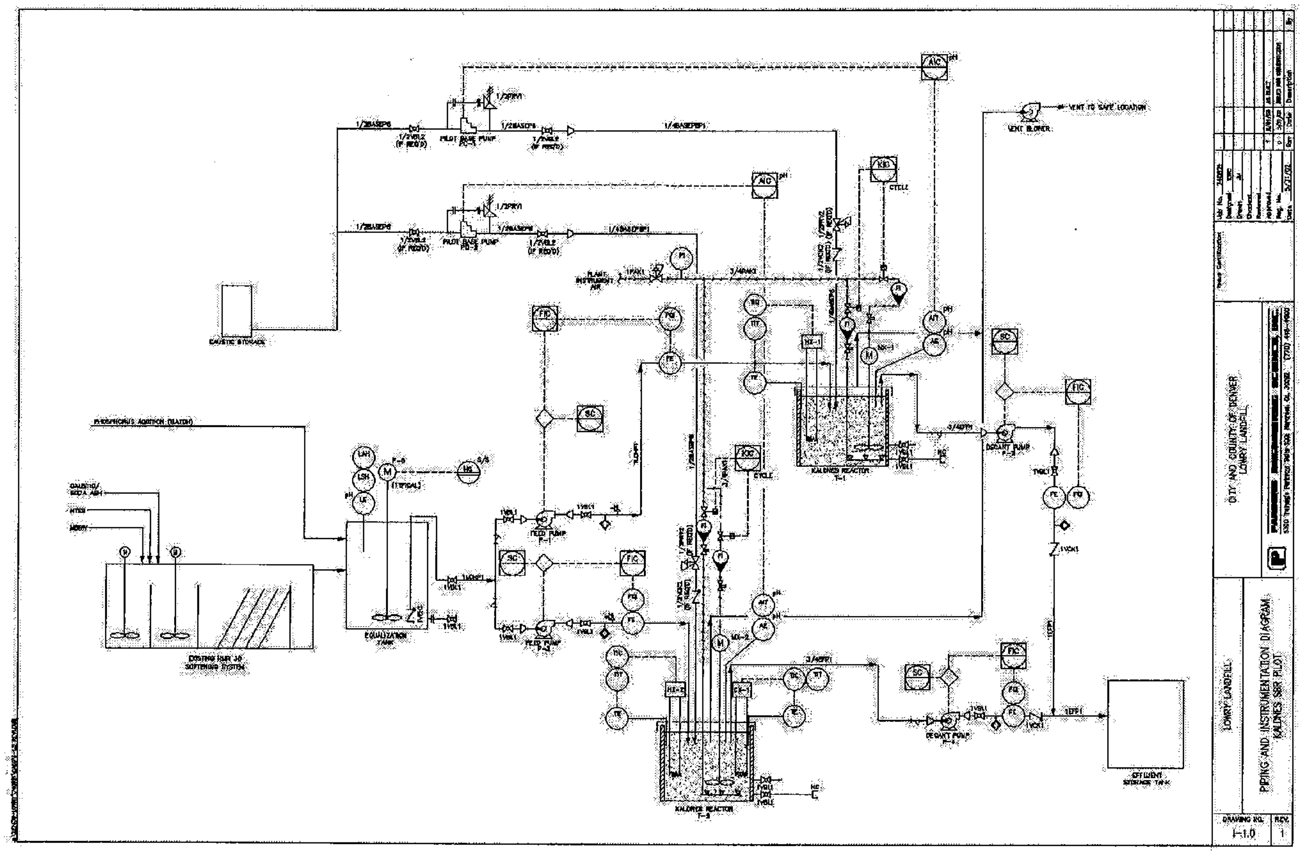
Figure 1: Pilot Reactor P&ID



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Feed was added with a variable-speed rubber-impeller centrifugal pump (ITT Jabsco) capable of delivering 0.3 to 1.5 gpm. The flow rate was monitored with an inline magnetic flow meter (Rosemount). The system PLC used the flow measurement to control pump speed. After the settle period, effluent was removed by a self-priming rubber-impeller centrifugal pump (ITT Jabsco) capable of 1 to 5 gpm. The pump was attached to a pipe that was lowered into the top of the tank to the desired effluent volume for the loading being tested in SBR operation. The down pipe was placed midway down the tank straight side of the reactor for the continuous flow tests (described below).

Reactor pH and temperature were continuously monitored throughout the pilot study using on-line temperature compensated pH meters (Rosemount). pH control was provided by the PLC, which turned a chemical metering pump (Pulsfeeder) on and off to supply the reactors with 25-percent NaOH to maintain a pH setpoint of 7.0 during the latter stages of testing.

During the Pilot Study, it was determined that denitrification was not possible due to carry over of dissolved oxygen from the aeration cycle; insufficient BOD was provided to the bacteria to remove the excess oxygen. Therefore, after 5.5 months of operation, the treatment system was converted to continuous flow reactors for the duration of the Pilot Study.

Analysis

Sample analysis was split between several laboratories. COD, ammonia, dissolved oxygen, pH, and solids/settling measurements were primarily performed in the field, with some verification by Severn Trent Laboratories (STL) in Denver, CO. Ammonia and dissolved oxygen were performed by ion selective electrode. COD was performed using high range (0-1500 mg/L) HACH vials. Initially the CODs were performed per the HACH standard method; however, it was discovered that the chlorides, bromides and ammonia contained in the groundwaters caused an overestimation of the COD due to oxidation in the COD vials(Belkin et al., 1992; Kim, 1989). Therefore, the COD method was adjusted to minimize the interference. All other parameters were measured using Standard Methods.

TOC, nitrate, nitrite, TKN, BOD_5, TDS, and THF were measured by STL using EPA standard methods. 1,4-dioxane measurements were conducted by Parsons and Zymax (San Luis Obispo, California) using EPA method 8021B.

PROCESS WATER CHARACERISTICS

Characteristics of the influent feed to the Pilot Study reactors (30/70 NTES/NBBW Blend) are summarized in Table 1.

Between November 2, 2002 and August 28, 2003, feed water processed through the pilot system was prepared in a batch mode and stored in the Pilot Equalization Tank on a regular basis. During the batch process, the NTES and NBBW groundwaters were blended in the softening tank of the existing WTP where caustic was added to raise the pH to 10.5. Solids were precipitated in the existing WTP clarifier. After softening, the water's pH was adjusted to 8.0 and pumped to the Pilot Equalization Tank (referred to as the "Blend Feed").

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TABLE 1: INFLUENT CHARACTERISTICS

Parameter	Units	Blended Feed
Flow	gpm	0.4-0.75
1,4--dioxane	µg/L	6,400-12,000
THF	µg/L	13,500-25,000
Soluble COD	mg/L	150-230
TOC	mg/L	62-92
TDS	mg/L	4300-5000
Ammonia	mg-N/L	80-160
Nitrite	mg-N/L	0.1-3.0
Nitrate + Nitrite	mg-N/L	10-19

Between November 2, 2002 and August 28, 2003, feed water processed through the pilot system was prepared in a batch mode and stored in the Pilot Equalization Tank on a regular basis. During the batch process, the NTES and NBBW groundwaters were blended in the softening tank of the existing WTP where caustic was added to raise the pH to 10.5. Solids were precipitated in the existing WTP clarifier. After softening, the water's pH was adjusted to 8.0 and pumped to the Pilot Equalization Tank (referred to as the "Blend Feed").

Organic Loading:

The Bench Tests showed that a large heal of COD remained in the effluent after treatment; 50% in the Blend reactors and up to 70% of the COD applied to the NTES reactors. This may be a residual affect of the inorganic inhibition of the COD test. Therefore, for the Pilot Test, Parsons defined the organic loading based strictly on the COD associated with 1,4-dioxane and THF. This was done because 1) the majority of the COD removed in the system can be attributed to 1,4-dioxane and THF removal and 2) 1,4-dioxane and THF could be measured independently from COD. The loading due to 1,4-dioxane and THF COD was calculated using the theoretical CODs for 1,4-dioxane and THF of 1.82 and 2.44 gram per gram COD, respectively.

RESULTS

Startup

The Pilot reactors were seeded prior to beginning operation to insure sufficient biomass for oxidation. 30-gallons of nitrifying activated sludge from the Denver Metropolitan Wastewater Reclamation Facility (Metro) was used as seed in each reactor. The initial fill of the Pilot reactor consisted of:

1. Kaldnes® media to 50-percent of the volume of the reactor
2. Approximately 30 gallons RAS from Metro; and
3. Blended waste to fill the reactor to capacity.

The primary objective of the startup period (September 7, 2002 to October 22, 2002) was to begin biomass attachment to the Kaldnes® media. To increase biomass development, additional COD was added to the reactors in the form of dog food. During the startup period the reactors

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were run in a batch mode to maintain good contact between the suspended biomass and the media. The dog food was added periodically and a batch was allowed to run until the COD dropped below 100 mg/L. The process was repeated for a month to allow biomass to grow on the media. Then the reactors were switched to SBR operation and the dog food supplements were discontinued. The average performance of the reactors during Startup and Acclimation are shown in Table 2.

Acclimation

As defined here, the period between startup and consistent treatment is acclimation. Acclimation of the reactors occurred between October 23, 2002 and February 13, 2003. The reactors were operated as SBRs and process water feed batches were made once every two weeks. During acclimation, both reactors experienced periods of poor performance, typically following sloughing of biomass from the media. Figure 2 shows the reactor performance with respect to the changing of the feeds and the media solids sloughing events. Figure 3 shows that the sloughing was likely caused by feed/starve cycles of the biomass due to THF biodegradation in the Pilot Equalization Tank. In order to reduce the degradation of THF in the EQ tank, the feed batch frequency was increased to once weekly on February 13, 2003. A further refinement was implemented in April 2003 where the volume of each batch of feed was reduced, eliminating excessive carryover from the previous batch. This feed procedure was continued while the Blend water was being tested.

Table 2 shows that the dissolved oxygen (DO) during the anoxic cycle averaged greater than 2 mg/L during acclimation. This was likely due to excessive carryover of oxygen from the previous aeration cycle coupled with the low organic carbon concentration in the feed. Due to the oxygen concentration, denitrification was inhibited. Since there are no permit limits for nitrogen and 1,4-dioxane degradation was not being affected, the anoxic cycle was removed from SBR operation in December 2002.

During acclimation the reactors were tested for removal efficiencies of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). In order to get a full understanding of the processes occurring in the reactors, samples were collected from the reactor feed, each reactor effluent, and from each reactor's off-gas ventilation system. VOC and SVOC samples were collected several times in January 2003. Due to the presence of high concentrations of 1,4-dioxane and THF, elevated detection limits masked the presence of other VOCs in the feed and effluent waters (data not shown).

The off-gas was sampled using 8-hour Summa canisters on December 6, 2002 and a thermal anemometer for flow measurement. Based upon the gas flow rates exiting the reactors, it was determined that less than 0.5% of the 1,4-dioxane was being removed by volatilization. This is to be expected since 1,4-dioxane have low Henry's Law Coefficients.

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Table 2: Average Reactor Performance During Startup And Acclimation

Parameter	Units	Startup		Acclimation	
		09/07/02 - 10/22/02		10/23/02 - 02/13/03	
		Reactor 1	Reactor 2	Reactor 1	Reactor 2
Influent					
Flow	(mL/min)	Batch Operation		0.65	
SCOD	(mg/L)	N/A	N/A	187	
TCBOD	(mg/L)	N/A	N/A	20	
SCBOD	(mg/L)	N/A	N/A	10	
TOC	(mg/L)	N/A	N/A	81	
TDS	(mg/L)	N/A	N/A	4779	
NH_3	(mg-N/L)	N/A	N/A	127	
NO_2	(mg-N/L)	N/A	N/A	1.01	
$NO_2 + NO_3$	(mg-N/L)	N/A	N/A	16.5	
TSS	(mg/L)	N/A	N/A	95	
pH	(S.U.)	N/A	N/A	7.83	
Phosphorus	(mg-P/L)	N/A	N/A	9.5	
1,4-dioxane	(ug/L)	19281		9828	
THF	(ug/L)	N/A	N/A	18909	
Anoxic Cycle					
pH	(S.U.)	N/A	N/A	6.3	6.4
DO	(mg/L)	N/A	N/A	2.1	2.1
ORP	(mV)	N/A	N/A	207	222
Temperature	(°C)	N/A	N/A	26.1	24.2
NH_3	(mg-N/L)	N/A	N/A	47.8	47.7
NO_2	(mg-N/L)	N/A	N/A	8.0	13
$NO_2 + NO_3$	(mg-N/L)	N/A	N/A	23.7	24.3
Aerobic Cycle					
MLSS	(mg/L)	2241	2020	723	550
MLVSS	(mg/L)	N/A	N/A	347	229
Media Solids	(g/m^2)	N/A	N/A	3.98	3.45
pH	(S.U.)	7.1	7.3	6.4	6.5
DO	(mg/L)	7.0	5.7	5.1	5.1
Temperature	(°C)	24.4	25.1	25.8	24.2
SVI		123	105	31	16
OUR	(mg/L*min)	0.64	0.33	0.20	0.17
Organic Loading	(g D&T COD/g TS*d)	N/A	N/A	0.080	0.080
Effluent					
SCOD	(mg/L)	369	497	124	143
TCBOD	(mg/L)	222.0	313.0	6.8	9.6
SCBOD	(mg/L)	N/A	N/A	3.8	4.4
TOC	(mg/L)	149.0	165.0	52.0	61.0
NH_3	(mg-N/L)	137	127	52	52
NO_2	(mg-N/L)	18.0	5.0	3.3	7.8
$NO_2 + NO_3$	(mg-N/L)	25.0	6.0	29.0	29.0
TSS	(mg/L)	N/A	N/A	52	85
VSS	(mg/L)	N/A	N/A	21	34
pH	(S.U.)	7.1	7.3	6.2	6.2
Phosphorus	(mg-P/L)	35.0	21.0	6.6	7.0
1,4-dioxane	(ug/L)	5725.0	5342.0	2763.0	1914.0
THF	(ug/L)	N/A	N/A	725.0	1223.0

Notes: N/A – Not Analyzed

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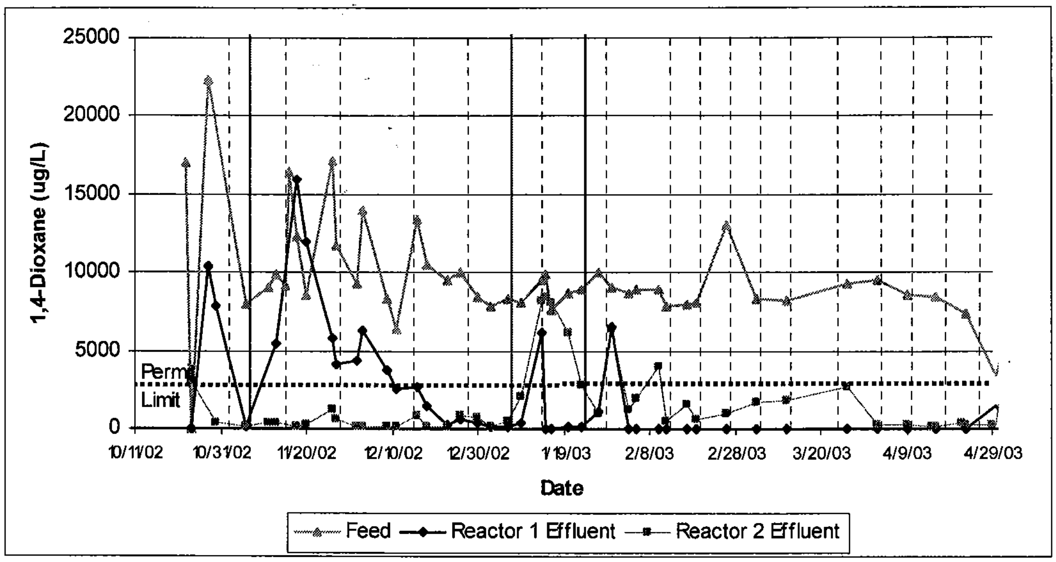
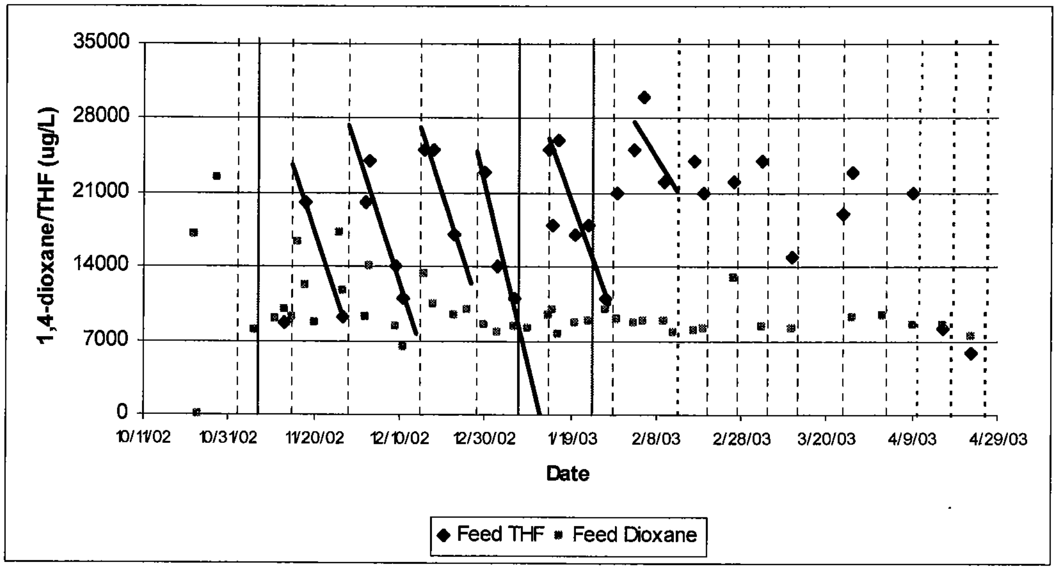
Figure 2: 1,4-dioxane Treatment Issues



Notes: Solid vertical lines denote sloughing events.
Dashed vertical lines denote feed changes.

Figure 3: Feed 1,4-dioxane and THF Decline



Notes: Solid vertical lines denote sloughing events.
Dashed vertical lines denote feed changes.
Solids diagonal lines denote slope of the THF data in that feed cycle.

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SBR Operation

After acclimation the reactors were allowed to run for two months in SBR mode to verify that the system could consistently treat the Blend waters. Table 3 shows the average performance characteristics for the two reactors during this period. The extended testing duration verified reactor performance in addition to confirming the previous sloughing events were an artifact of the test approach. As can be seen in Figures 4 and 5, THF and 1,4-dioxane degradation were consistent, with no sloughing events. Reactor 1, which had been operating well before the change in feed procedures, continued to operate at greater than 98-percent removal rates for both 1,4-dioxane and THF. Reactor 2, which had just experienced a sloughing event prior to the change in feed procedure recovered in a little more than a month and returned to greater than 98-percent removal rates.

Figure 6 shows how the mass of attached solids changed after the acclimation period. Both reactors exhibited an increase in attached solids , which eventually leveled off between 2,000 to 2,500 g of solids per reactor. This is equivalent to a mass per media surface area between 6 to 8 g/m^2, compared to the design value of 7 g/m^2. However, suspended solids concentrations were consistently less than 400 mg/L, and were continuing to decline as the study progressed. This was primarily because the suspended solids settled very poorly with a large portion remaining dispersed throughout the reactor during the decant cycle. Therefore, a large mass of suspended solids was removed in each decant.

Continous Flow Operation

After two months of operation as SBRs, the reactors were converted to continuous flow bioreactors. This greatly simplified the control and operation of the reactors, as well as allowed the reactors to operate without having the transient concentration spikes associated with batch feeding.

The reactors were converted in a staggered sequence to evaluate any change in reactor performance. Reactor 2 was converted on April 22, 2003 and Reactor 1 was converted on May 14, 2003. Increased 1,4-dioxane effluent concentrations from both reactors were noted after conversion of Reactor 2 that was attributed to low feed concentrations. No change in 1,4-dioxane degradation was attributable to the conversion. However, effluent ammonia concentrations in each reactor declined after changing to continuous operation, and there was a corresponding increase in nitrate during the same period. This is likely because of enhanced nitrification due to the steady application of feed and lower bulk concentrations of contaminants that are typical with continuous feed reactors.

At the same time the reactors were converted from SBR to continuous flow mode, pH control was added to each reactor to evaluate its effect on reactor performance. Pumps dosing 25-percent sodium hydroxide were added to each reactor. Data collected in August 2003, indicated that the reactors were utilizing 1,800 mL/day of the caustic. These data were taken while both reactors were still nitrifying, requiring the use of additional alkalinity.

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TABLE 3: AVERAGE REACTOR PERFORMANCE DURING SBR AND INITIAL CONTINUOUS OPERATION

Parameter	Units	SBR		Continuous	
		02/14/03 - 05/14/03	02/14/03 - 04/22/03	05/14/03 - 07/11/03	06/01/03 - 07/11/03
		Reactor 1	Reactor 2	Reactor 1	Reactor 2
Influent					
Flow	(mL/min)	0.68		0.41	
SCOD	(mg/L)	201		N/A	
TCBOD	(mg/L)	15		N/A	
SCBOD	(mg/L)	10		N/A	
TOC	(mg/L)	76		71	
TDS	(mg/L)	4450		4650	
NH_3	(mg-N/L)	115		108	
NO_2	(mg-N/L)	0.22		1.6	
$NO_2 + NO_3$	(mg-N/L)	11.3		8.8	
TSS	(mg/L)	22		16	
pH	(S.U.)	7.6		7.9	
Phosphorus	(mg-P/L)	5.0		N/A	
1,4-dioxane	(ug/L)	9056		8341	
THF	(ug/L)	20410		17760	
Anoxic Cycle					
pH	(S.U.)	N/A	N/A	N/A	N/A
DO	(mg/L)	N/A	N/A	N/A	N/A
ORP	(mV)	N/A	N/A	N/A	N/A
Temperature	(°C)	N/A	N/A	N/A	N/A
NH_3	(mg-N/L)	N/A	N/A	N/A	N/A
NO_2	(mg-N/L)	N/A	N/A	N/A	N/A
$NO_2 + NO_3$	(mg-N/L)	N/A	N/A	N/A	N/A
Aerobic Cycle					
MLSS	(mg/L)	363	102	107	48
MLVSS	(mg/L)	199	36	61	40
Media Solids	(g/m^2)	5.3	5.9	7.1	8.2
pH	(S.U.)	6.3	6.4	7.0	7.1
DO	(mg/L)	9.8	12.5	3.6	5.6
Temperature	(°C)	25.5	24.2	25.7	14.8
SVI		20	13	N/A	N/A
OUR	(mg/L*min)	0.17	0.17	0.21	0.22
Organic Loading	(g D&T COD/g TS*d)	0.064	0.069	0.061	0.050
Effluent					
SCOD	(mg/L)	127	146	N/A	N/A
TCBOD	(mg/L)	5.5	8.2	N/A	N/A
SCBOD	(mg/L)	2.8	3.9	N/A	N/A
TOC	(mg/L)	50	58	52	51
NH_3	(mg-N/L)	51	53	32	108
NO_2	(mg-N/L)	0.37	0.27	0.38	0.02
$NO_2 + NO_3$	(mg-N/L)	28	28	67	33
TSS	(mg/L)	30	18	198	234
VSS	(mg/L)	15	9.5	138	165
pH	(S.U.)	6.2	6.0	6.98	7.05
Phosphorus	(mg-P/L)	4.6	4.5	N/A	N/A
1,4-dioxane	(ug/L)	150	1003	57	83
THF	(ug/L)	5	118	46	212

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Figure 4: 1,4-dioxane Profiles, Post Acclimation

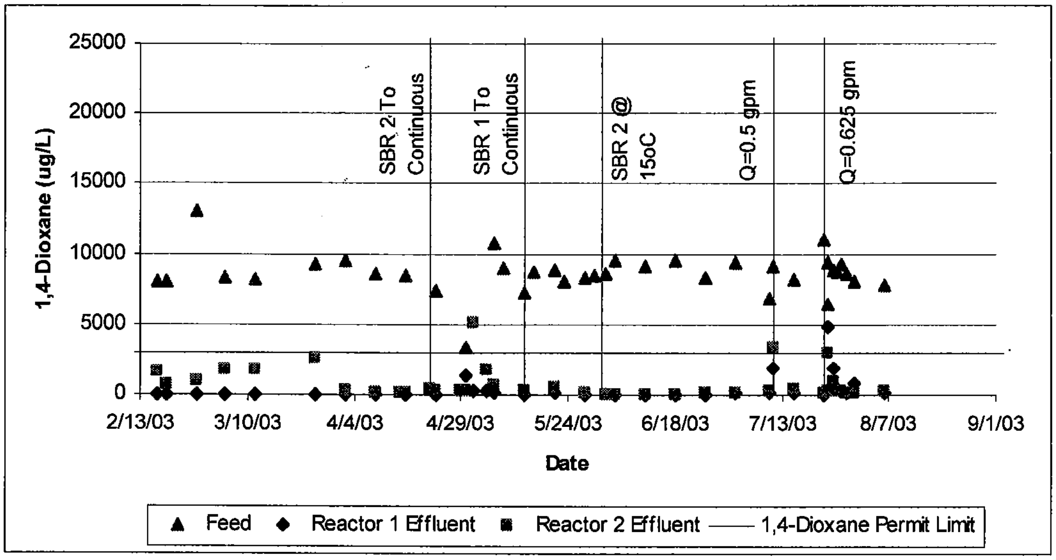

Figure 5: THF Profiles, Post Acclimation

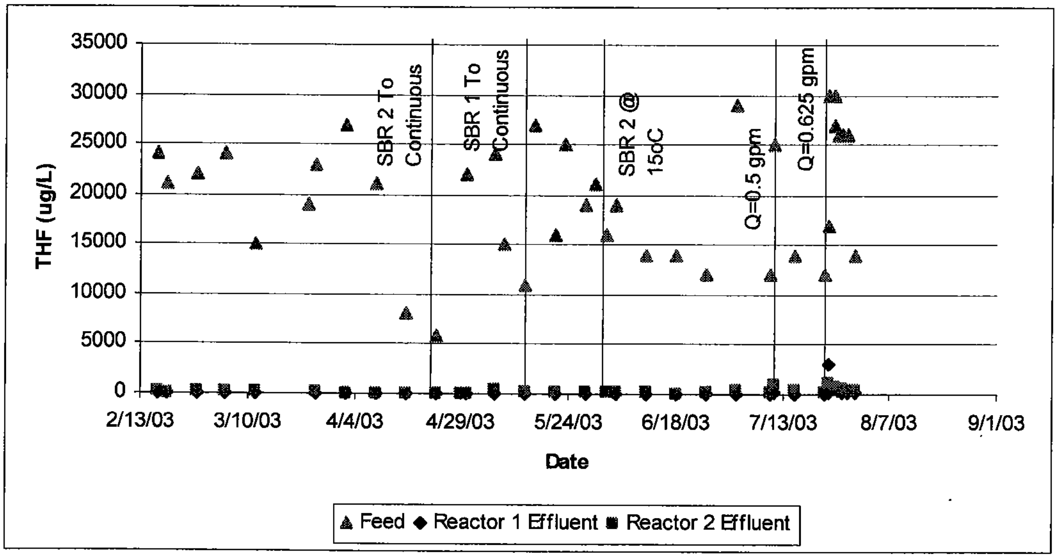

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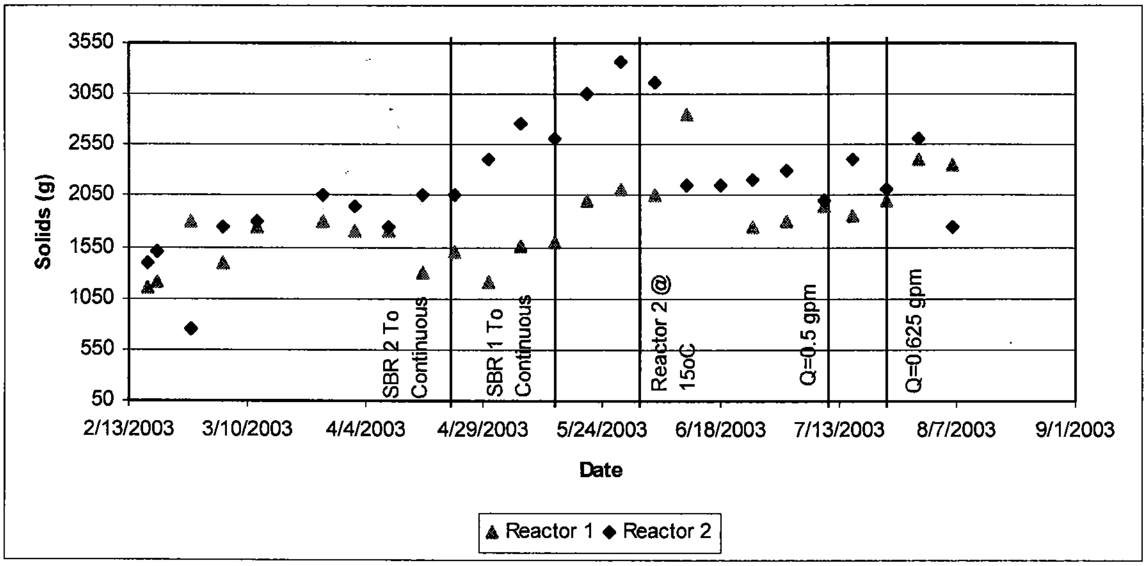
Figure 6: Mass of Attached Solids, Post Acclimation



Temperature Variation: With both reactors operating at steady state conditions, the operating temperature of Reactor 2 was reduced from 25 °C to 15 °C. The temperature was reduced by 2 °C per day, with the reactor reaching 15 °C on June 1, 2003. Reactor 2 operated for five weeks at the new condition to show stability and to verify that no adverse affects would be seen from changing the temperature. Reactor 1 acted as a control during this period. At the feed conditions tested, there was no discernable effect on 1,4-dioxane or THF removal by lowering the temperature of Reactor 2.

Lowering the temperature did reduce nitrification efficiencies, resulting in higher effluent ammonia and lower effluent nitrate concentrations (Figures 7, 8, and 9). The increase in effluent ammonia due to decreased nitrification was not considered an adverse affect since 1) there is no nitrogen limit on the facility discharge permit and 2) the increased ammonia concentration appeared to have no inhibitory affects on 1,4-dioxane and THF degradation.

Volumetric Loading Variation: Subsequent to the temperature change discussed above, the organic loading to the reactors were increased to evaluate its effect on reactor performance. Since the composition of the feed was fixed at a constant blend ratio, the organic loading could only be increased by increasing the volumetric flow rate to the system; thereby applying more mass of 1,4-dioxane and THF over a shorter time period. Step changes were made to the flow rate to evaluate recovery time in each reactor.

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Figure 7: Ammonia Profile, Post Acclimation

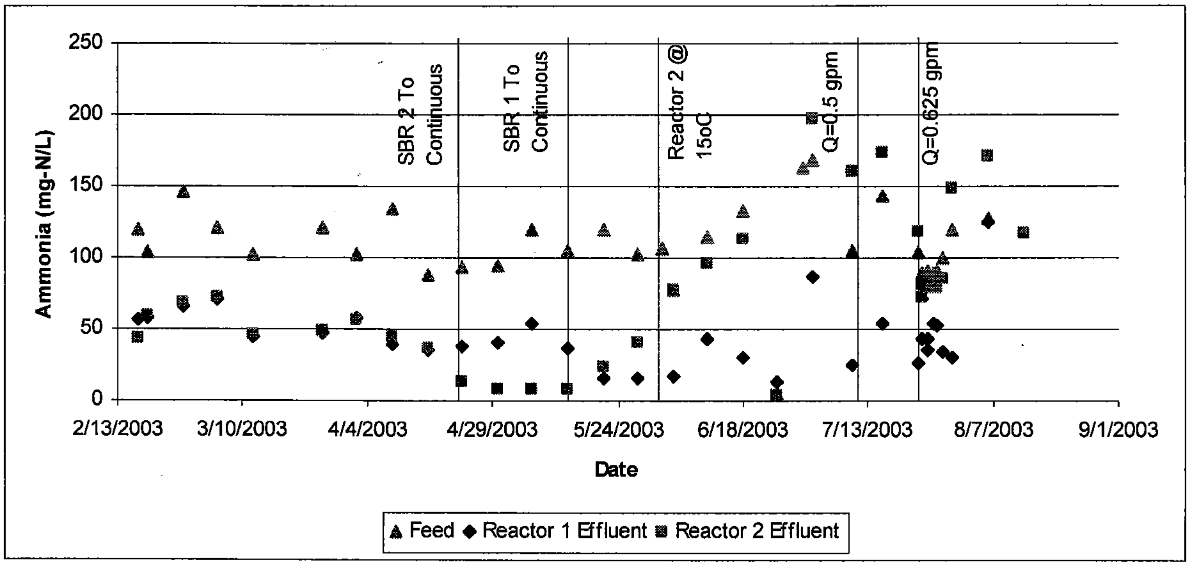

Figure 8: Nitrite Profile, Post Acclimation

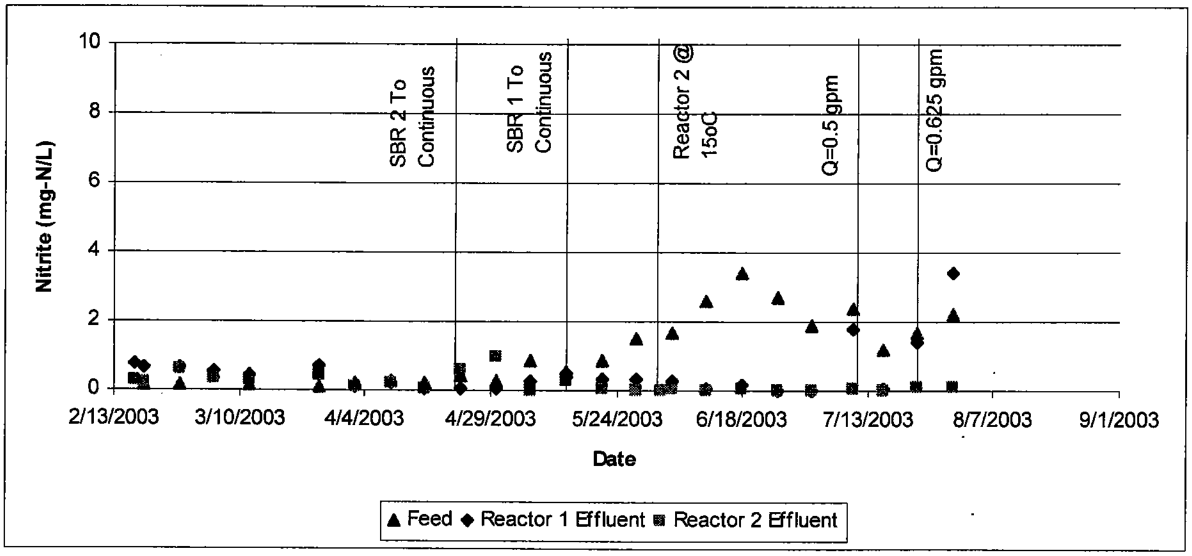

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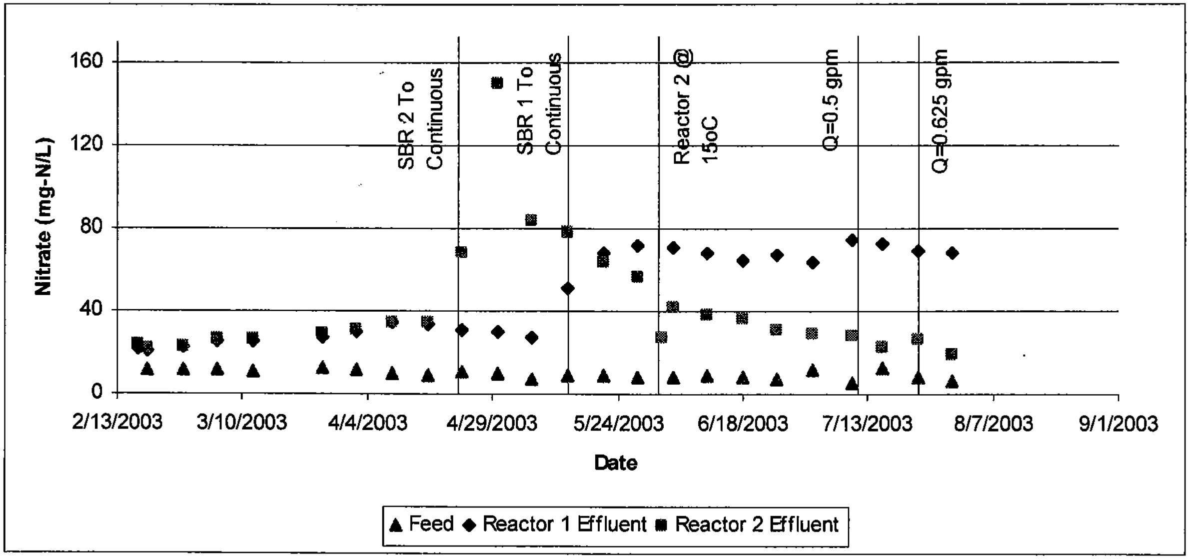
Figure 9: Nitrate + Nitrite Profile, Post Acclimation



A 25% increase in organic loading was made on July 11, 2003 (0.4 to 0.5 gpm) Each reactor showed the expected spike in effluent 1,4-dioxane concentrations, with 1,4-dioxane degradation efficiencies dropping from greater than 95% in both reactors to 79% in Reactor 1 and 64% in Reactor 2. A second 25% increase occurred on July 23, 2003 (0.5 to 0.63 gpm), and showed a similar trend in effluent 1,4-dioxane concentrations with increased performance in Reactor 2 (efficiencies only dropping to 89%). Both reactors showed complete recovery to nominal treatment efficiencies in less than five days after both adjustments. THF removal efficiencies declined slightly (2 to 3%) during these same periods.

With increased organic loadings, higher bio-solids loadings were expected on the media. Figure 6 shows that the solids in each reactor did appear to be increasing during the period of increased loading, but there were insufficient samples to make a clear correlation. Figure 6 also shows that the bio-solids in Reactor 2 were consistently higher than Reactor 1 during this period as well, which may explain why Reactor 2 was better able to cope with the second step increase in loading.

Oxygen Uptake Rates

Oxygen uptake rate (OUR) is a measure of bacterial metabolism. As the OUR increases, the faster the biomass is growing and using the food provided. Figure 10 shows that there was little change in the measured OURs for each reactor since acclimation. Note that the OURs in Figure 10 are adjusted with respect to the mass of biomass present in each reactor.

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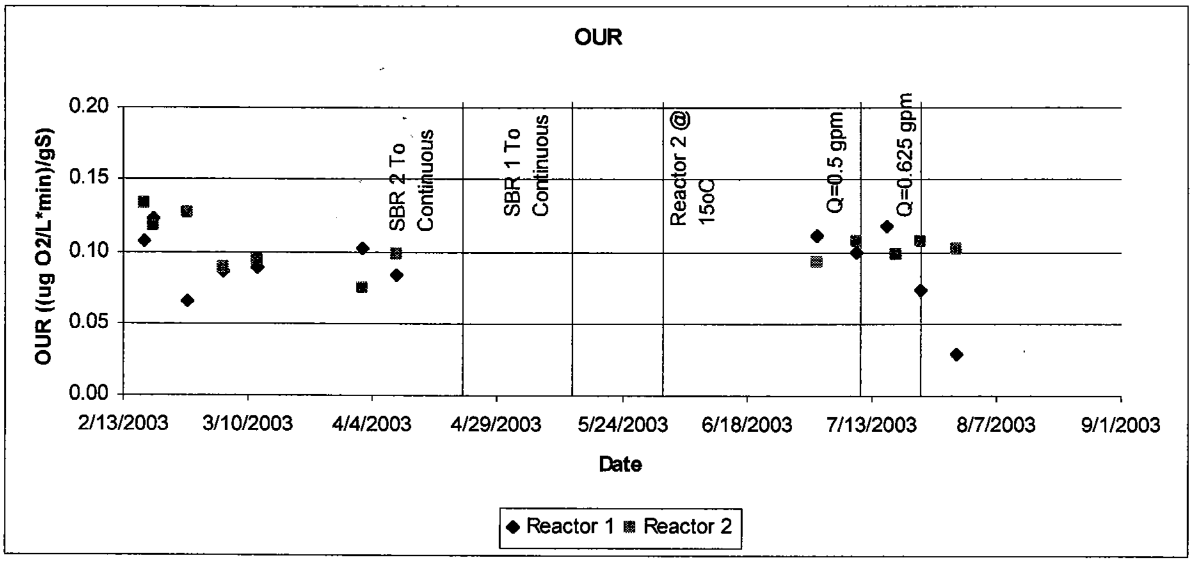
Figure 10: Oxygen Uptake Rate, post Acclimation



DISCUSSION

SBR Operation

At the start of the steady state period of SBR operation, the reactors had been operating for five months, with varying degrees of success. There was a good base of biomass on the media, and it was proving adequate for 1,4-dioxane degradation at the operating conditions. Once provided with a stable feed of THF, the reactors began to operate as expected from the bench scale tests. It was not surprising for the reactors to operate poorly when under-loaded, as the bench scale tests showed that 1,4-dioxane degradation decreased when the organic loading was too low (data not published). This further supports the theory that the degradation of 1,4-dioxane is linked to THF as a form of cometabolism. The THF provides the primary source of energy for the bacteria and 1,4-dioxane is degraded by the THF enzymes. Therefore, if there is too little THF, then fewer enzymes are produced and little 1,4-dioxane will be degraded.

Figures 11 and 12 show the organic loadings of the two reactors after the acclimation period. The organic loading in the two reactors was inconsistent during SBR operation, primarily because of a combination of variability of the feed concentrations and the increasing biomass on the media. As the media solids increased, the organic loading decreased, such that the average organic loadings during the SBR operation were 0.064 and 0.069 grams of dioxane and THF as COD/grams of Total Solids * day (g D&T COD/g TS*d), for Reactors 1 and 2 respectively.

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Conversion to Continuous Flow

The SBRs were converted to continuous flow reactors because:

1. Nitrification was not achieved;
2. Continuous reactors are less complex then SBRs;
3. Continuous flow reactors typically result in a more consistent, low bulk concentration compared to SBRs, possibly reducing inhibition; and
4. Continuous flow reactors eliminate the concentration transients that are inherent in batch feeding.

When changing the reactors from SBR to continuous flow mode, an effort was made to maintain the organic loading level to minimize the number of changed variables so that any changes in operation could be attributed to the change is flow regime rather than changes in organic loading.

However, the media solids continued to increase in each reactor, causing the organic loading to drop during this period. The average organic loadings during the initial continuous flow operation were 0.061 and 0.050 g D&T COD/g TS*d, for Reactors 1 and 2 respectively.

Throughout continuous flow operation the removal of 1,4-dioxane and THF consistently exceeded 95-percent. When ncreases in volumetric loading were implemented, corresponding increases in organic loading were expected. However, because of a combination of decreased THF feed concentration over time and increased media solids, the organic loading only increased slightly during the adjustments.

Figure 11: Reactor 1 Organic Loading

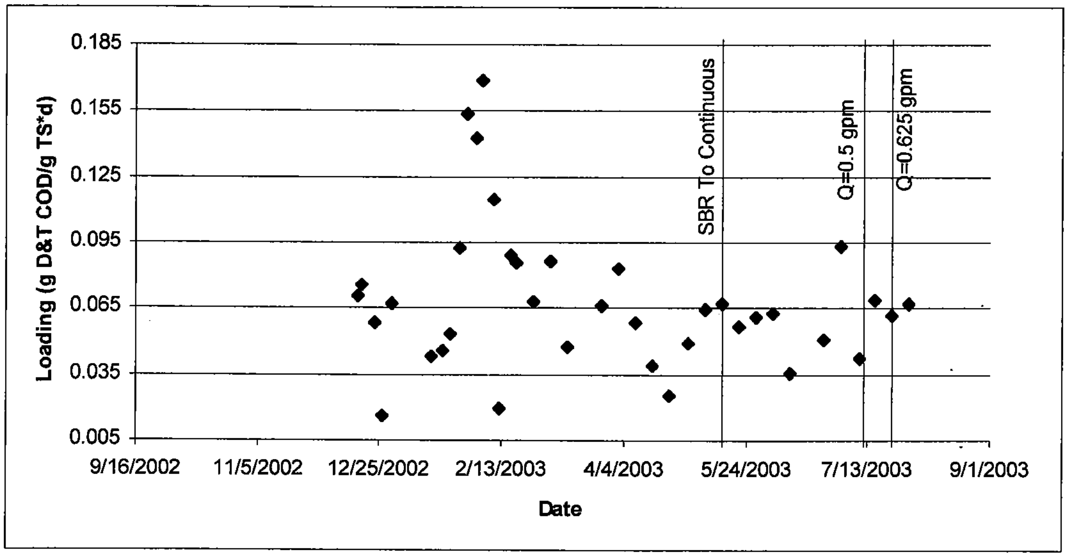

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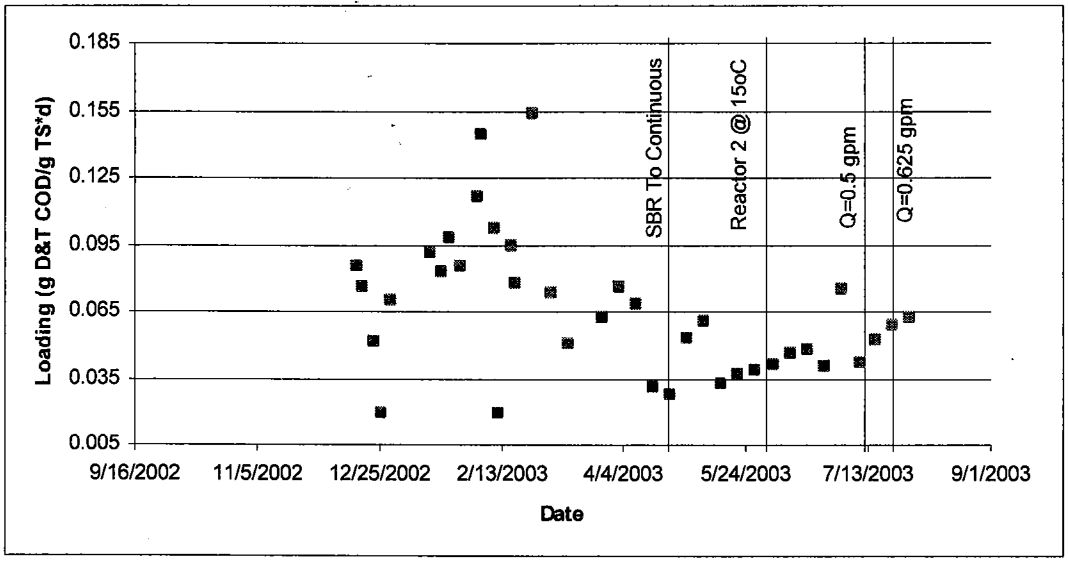
Figure 12: Reactor 2 Organic Loading



1,4-Dioxane Degradation By Cometabolism

Research at North Carolina State University (NC State) (Zenker et al., 2000) concluded that THF acts both as a catalyst and competitive inhibitor for 1,4-dioxane degradation. The NC State research showed that their 1,4-dioxane degrading biomass used THF for cell growth and energy, but exhibited no removal of 1,4-dioxane when THF was not present. However, the NC State researchers also discovered that when THF was present at high concentrations it was degraded preferentially, with little 1,4-dioxane degradation until the THF concentration fell to low levels. This is in direct opposition to the biomass grown by Sock (1993); which, while initially fed with THF and 1,4-dioxane, was able to degrade 1,4-dioxane as a sole substrate when the THF was discontinued.

The spikes of effluent 1,4-dioxane that accompanied the two step increases in volumetric loading (See Figures 4 and 5), coupled with the much lower increases in effluent THF concentrations indicates that the biomass in the pilot reactors more closely resembles that researched by Zenker, et.al. When the loading was increased, an additional mass loading of THF and 1,4-dioxane would have been applied to the system, causing an increase in the bulk concentration of both chemicals. The data suggests that the biomass absorbed the increase in THF very quickly, but not the 1,4-dioxane. However, when the biomass had adapted to the increased mass of THF, the 1,4-dioxane was quickly removed.

STUDY OBJECTIVE RESULTS

As previously stated in this report, the pilot study had four primary objectives:

1. Evaluate the sustainability and robustness of 1,4-dioxane degradation;
2. Assess the effect of temperature on the degradation of 1,4-dioxane;
3. Assess the effect of organic loading on the stability of 1,4-dioxane degradation; and
4. Provide criteria for sizing and design of a full-scale biological system.

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Each of these objectives was met during the Pilot Study and are discussed below.

Sustainability and Robustness

After start-up and acclimation, the reactors were run continuously for seven months. During that time, the only excursions above the effluent 1,4-dioxane limit could be attributed directly to changes in the feed composition or flow. This long period of consistent treatment shows that the biomass is stable. The quickness of response by each reactor to the step increases in volumetric loading, less than five days for each change, shows the robustness of the biological system.

The implementation of the Pilot Study required that the feed be made in batches, with the variability that came with the batch-making procedure. Additional variability was introduced by the unintended, and uncontrollable, biodegradation occurring in the Pilot Equalization Tank. These two variables caused the reactors to experience a higher feed variability than would be anticipated in a full scale system because the full scale system will receive a continuous feed directly from the groundwater extraction trench without the need for an EQ tank. Site experience has indicated that groundwater quality changes tend to be more subtle, as compared to what was observed in the storage tank. The gradual changes in process water feed concentrations should be absorbed by a full scale system without comprising effluent quality.

The one exception to this would be if the THF concentrations in the NTES groundwater were to decrease below that which can sustain the biomass or 1,4-dioxane cometabolism. This is a possibility as more NTES water is pumped and the contaminants are attenuated. Different approachs can be used in a full scale system to diminish the impact of lowered THF concentrations. One such approach would be to add supplemental THF through a chemical addition system. A more efficient way to deal with this possible change in water quality is to design the full scale system with the ability to vary the reaction volume and the percentage of media fill. By lowering the fill percentage of reaction volume, you essentially increase the organic loading per mass of biomass, such that even at lower concentrations of feed THF the biomass is not starved.

Temperature Effects

After changing to continuous feed operation, Reactor 2 was decreased to an operating temperature of 15 °C. This is the typical temperature of the process waters in the WTP. There was little to no affect on 1,4-dioxane degradation with the decrease in temperature. However, Reactor 2 quickly lost its ability to nitrify, allowing ammonia to pass through the system untreated. Since there is no nitrogen limits on the existing WTP, and the ammonia concentration is below that which will inhibit biological growth, the loss of nitrification is acceptable.

Organic Loading

Organic loadings during the Pilot Study ranged from 0.05 to 0.10 g D&T COD/g TS*d. The changes in organic loading were followed by quick adaptation by the reactors. At no time did the organic loading exceed the capacity of the reactors. Based on the bench results, lower (0.04) and higher loadings (0.15) are possible.

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CONCLUSIONS

The following conclusions were made based on the results of the Pilot Study:

1. 1,4-dioxane can be degraded to greater than 95-percent efficiency consistently in the process waters at organic loadings of 0.04 to 0.075 g D&T COD/g TS*d.
2. Biodegradation of 1,4-dioxane at 15 °C is possible with little impact on removal efficiencies.
3. 1,4-dioxane is not removed by volatilization.
4. Reactor operation at 15 °C inhibits nitrification.
5. Alkalinity is required to fully nitrify at 25 °C.
6. Too little feed THF can result in reduced 1,4-dioxane degradation efficiency.
7. Instantaneous increases in loadings of 25-percent will result in 2-3 days decreased 1,4-dioxane degradation efficiency, with possible effluent concentrations above the permit limit.

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