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APPLICATION OF BIOREACTOR SYSTEMS TO LOW-CONCENTRATION PERCHLORATE-CONTAMINATED WATER (RFP 2530)

PROPOSAL SUBMITTED TO

AMERICAN WATER WORKS ASSOCIATION RESEARCH FOUNDATION

May 4, 1998

Submitted by

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with participation from

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MONTGOMERY WATSON

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PROPOSAL COVER WORKSHEET

Project Title: Application Of Bioreactor Systems To Low-Concentration Perchlorate-Contaminated Water (RFP 2530)

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Participating Utilities

1. City of Riverside
2. Main San Gabriel Basin Watermaster
3. Southern Nevada Water Utility

AWWARF Funds Requested: $274,960

In-Kind Contributions: $92,083

Project Period: October 1, 1998 – September 30, 2000

TOTAL PROJECT BUDGET: $367,043

In-Kind* Support Worksheet for Participating Utilities and Other Participating Organizations

Name of Organization	Name of Contact	Letter of Support	Amount Specified in letter
Main San Gabriel Watermaster	Carol Williams	Yes	$10,000
City of Riverside	Bill Carnahan	Yes	$2,000
Southern Nevada Water Utility	David Rexing	Yes	$5,000
TOTAL IN-KIND			$17,000

*In-kind contributions from the research partners are not included in the table. They are: $3,000 from Montgomery Watson and $72,083 from Northwestern University

ABSTRACT

The objectives of this project are 1) to determine the mechanisms, kinetics, and requirements of biological perchlorate reduction, and 2) develop a reliable process that will produce a safe drinking water that meets all regulatory and aesthetic requirements.

Perchlorate has been detected in several ground surface waters at levels exceeding the State of California action level of 18 μg/L. Microbial reduction of perchlorate has been demonstrated and is the most promising alternative for achieving perchlorate destruction. However, many fundamental questions about microbial perchlorate reduction in the drinking-water setting remain unanswered.

Denitrifying bacteria, which reduce nitrate to gain energy, also reduce perchlorate. This is fortunate, because high levels of nitrate normally accompany perchlorate contamination. A supplemental electron donor must be provided to reduce the perchlorate, nitrate, and dissolved oxygen present. Methanol and ethanol have been used for perchlorate reduction in the past, but alternative supplements – particularly acetate and H_2 – offer cost, water quality, and regulatory benefits. In particular, the use of H_2 as the electron donor is mostly appealing because it eliminates the need for the addition of an organic chemical to the water.

?

MeOH
EtOH
Acetate
H_2

Our research will answer these fundamental questions:

very good

1. Does nitrate compete with perchlorate? How low must the nitrate concentration be driven to allow perchlorate reduction?
2. Is nitrate necessary for perchlorate reduction when present at sub mg/L levels.
3. At what concentrations does oxygen stop perchlorate reduction and how?
4. What is the most effective supplemental type and dose of the electron donor required to drive denitrification and perchlorate reduction: methanol, acetate, or H_2?
5. What is the rate-controlling mechanism and how can we describe its kinetics?
6. What is the effluent quality in terms of residual electron donor, reduction intermediates of ClO_4^-, NO_2^-, BDOC, and disinfection by-product precursors?
7. Are VOCs, such as TCE, reductively dechlorinated or inhibit perchlorate reduction?

Kinetics

The fundamental questions will be addressed by bench-scale experiments in completely mixed biofilm reactors. For supplementation with ethanol and acetate, we will construct porous-medium biofilm reactors. For H_2 supplementation, we will use our novel membrane biofilm reactor, which is now achieving outstanding denitrification for drinking water, and which has already been demonstrated to achieve perchlorate reduction. All of the information generated by the fundamental studies will be used to assess the engineering and economic feasibility of microbiological perchlorate reduction for drinking water. Key issues include post-treatment needs, scale-up, operability and reliability, capital and O&M costs, and design criteria. A specific outcome will be a plan for Phase II pilot testing.

Our proposed team includes Northwestern University and Montgomery Watson in cooperation with three water agencies from California and Nevada. We propose to conduct this project within a period of 18 months, followed by 6 months of draft and final project reports development. The project team has committed approximately $92,000 in in-kind contributions. With $275,000 contribution from AWWARF, the project budget is approximately $367,000.

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SECTION 1
PROJECT OBJECTIVES AND BACKGROUND

PROJECT OBJECTIVES

The objective of this project is investigate the feasibility of utilizing direct biological treatment as a means of removing perchlorate from contaminated drinking water sources. The project will focus on conducting bench-scale laboratory testing to investigate the fundamentals of biological treatment of perchlorate and to evaluate its applicability as a drinking water process.

PERCHLORATE BACKGROUND ISSUES

Perchlorate (ClO_4^-) has been detected in various California groundwaters at levels as high as 180,000 µg/L, in Colorado River water at 7 to 9 µg/L, and with some surface waters containing levels as high as 165 µg/L (California DPH, 1998). The problem was first discovered during a Superfund monitoring program in northern California in February 1997. Since then, perchlorate has been detected in more than 100 groundwater wells in California, Nevada, and Utah.

Perchlorate is a very strong oxidant (and is highly explosive) in its solid state. It is used as a solid rocket fuel in the form of ammonium perchlorate (NH_4ClO_4). It is also used as the propellant for fireworks and munitions. However, perchlorate is extremely stable when dissolved in water at concentrations as high as 100 mg/L. As a result of its well-defined use, the main source of perchlorate in the various groundwater and surface waters impacted can be traced to locations where ammonium perchlorate has been manufactured, tested, handled, or stored.

In very high doses, perchlorate has been used in medicine for the treatment of Graves' disease. As such, there is an abundance of health effects information on perchlorate. When ingested, perchlorate interferes with the ability of the thyroid gland to utilize iodine to produce thyroid hormones, which are an essential element of the body's growth and development. Studies conducted on humans (Stanbury and Wyngaarden, 1952) were used by the USEPA (1992) to evaluate the health risks associated with the ingestion of perchlorate. Based on this analysis, a reference dose (RfD) range of 0.0001 mg/kg/day to 0.0005 mg/kg/day was determined, which translates into a water level of 4 to 18 µg/L (assuming 2 L/day water consumption over a 70-year period). However, this information is based on acute effect of perchlorate, and great uncertainties remain regarding its chronic human health effects.

The California Department of Health Services adopted an action level of 18 µg/L for perchlorate in drinking water and recommended that water sources containing more than 18 µg/L perchlorate be taken off-line. As of October, 1997, 34 monitored wells contained greater than 18 µg/L. Twenty two of those wells were closed due to perchlorate contamination.

BIOLOGICAL TREATMENT OF PERCHLORATE

Currently, four treatment alternatives are actively being considered for removing perchlorate from groundwater (Montgomery Watson, 1997): 1) biodegradation, 2) membrane filtration, 3) removal with GAC, and 4) ion-exchange (IX). The utilization of biological treatment for the removal of inorganics from water is not new. For example, Appendix B includes a thorough literature review conducted by Bruce Rittmann (Proposed PI on this project) on Biological Denitrification of Drinking Water. The literature review illustrates that microbially catalyzed reduction of nitrate (NO_3^-) to nitrogen gas (N_2) is a practical and economically feasible treatment process. Biological reduction of perchlorate (ClO_4^-) to chloride ion (Cl^-) has been demonstrated by various researchers. The issue to be addressed is whether perchlorate reductions can be practical in a drinking water setting.

Using a suspended-growth biological process, Attaway and Smith (1983) and Attaway et al. (1996) identified a bacterium capable of reducing perchlorate to chloride: *Wolinella succinogenes HAP-1*. They hold a US patent on their process design (US Patent 5,302,285). However, the researchers were utilizing this bacterium for the reduction of perchlorate from levels as high as 3,000 mg/L. They achieved effluent perchlorate as low as 0.5 mg/L (500 μg/L),which is still orders of magnitude higher than the drinking water levels of interest.

For the past two years, the Aerojet Corporation also conducted research on biological perchlorate treatment using an upflow fixed-film process. The process utilizes Granular Activated Carbon (GAC) as a medium for growing and sustaining a bacterial biofilm. The fixed-film design allows the process to have a hydraulic detention time of about 12 to 24 minutes, which is quite reasonable for drinking water treatment. Aerojet's process has been reportedly tested for the removal of low-level perchlorate in groundwaters in Northern California, with the effluent perchlorate concentration maintained at or below the method detection limit of 4 μg/L.

Two factors complicate the use of biological treatment for perchlorate removal. First, when nitrate is present in the groundwater (which is the case in most of the contaminated groundwater wells), the biological removal of nitrate is more favorable and will have to be accomplished before perchlorate can be removed. Second, the process requires the addition of an electron donor at doses sufficient to achieve the reduction of nitrate and perchlorate. The Aerojet process utilized ethanol as the electron donor, which also served as the carbon source for the microorganisms. Methanol is another organic electron donor frequently added for denitrification. Both compounds are alcohols that are federally regulated, and methanol has acute health risks. Therefore, effluents produced by these donors could not be used for drinking purposes until the issue of residual methanol or ethanol is resolved or until an alternate electron donor replaces them. In order to avoid the above complications, we propose to evaluate acetate and hydrogen, as well as methanol, as electron donors. These choices emphasize production of a safe and aesthetically pleasing water.

SECTION 2
PROJECT DESCRIPTION

Similar to NO_3 reducta

PROJECT UNDERSTANDING

This project investigates and verifies the destruction of perchlorate in contaminated drinking water using biological reduction. The fundamentals of the process are straightforward in that, in the absence of oxygen, bacteria can utilize perchlorate as an electron acceptor, as long as water contains sufficient electron donors. The output energy from this process is used as the energy source for bacterial growth.

Perchlorate reduction is highly similar to the anoxic biological denitrification process in which nitrate is reduced by microorganisms to nitrogen gas. In fact, the majority of perchlorate-contaminated groundwaters in California also contain significant levels of nitrate. In these waters, perchlorate is present at less than 100 μg/L levels while nitrate is present at greater than 1 mg/L level – more than one order of magnitude difference. The experience of several researchers suggests that nitrate is a more favorable electron acceptor than perchlorate, and therefore will be biologically reduced before perchlorate. However, experience also suggests that the presence of nitrate (in the mg/L concentration range) is essential to sustaining an active bacterial population. As such, it is not clear at this time whether or not a bacterial population can be sustained with sub mg/L perchlorate concentration alone. Answering this question is essential to determining whether biological treatment is a viable process for the removal of perchlorate from groundwaters (or surface waters) that do not contain substantial levels of nitrate (for example, Colorado River water).

Due to the strong similarities between biological denitrification and biological reduction of perchlorate, we believe that the experience gained in the design of biological denitrification processes will be of great benefit to the evaluation of biological reduction of perchlorate. One of the main drawbacks of biological denitrification as practiced in the industry is the addition of methanol or ethanol as both the electron donor and the carbon source. When applied in drinking water treatment, the addition of these chemicals has many serious drawbacks. Therefore, in addition to the evaluation of various organic carbon sources such as methanol, nol, and acetate, we propose to evaluate the addition of H_2 as the electron donor to an autotrophic bacterial population that utilizes natural bicarbonate as the carbon source. We believe that utilizing this approach for biological perchlorate reduction provides the essential benefit of the elimination of the need for the addition of organic chemicals to the process.

This section first provides a brief review of denitrification and the developing options for denitrification of drinking water. A comprehensive review is provided in Appendix B. We identify the special roles played by perchlorate, nitrate, and the electron donor. We then conclude by assessing the feasibility of different approaches using a range of electron donors.

Denitrification Basics

Denitrification is a respiratory process in which the reduction of nitrate and nitrite to N_2 is coupled to electron-transport phosphorylation and energy generation. Nitrate (NO_3^-) or nitrite (NO_2^-) is reduced sequentially to nitric oxide (NO), nitrous oxide (N_2O), and nitrogen gas (N_2). Each stepwise reduction of nitrogenous oxides is catalyzed by a specific enzyme, namely nitrate reductase (NaR), nitrite reductase (NiR), nitric-oxide reductase (NOR), and nitrous-oxide reductase (N_2OR) (Ye et al., 1994). All the denitrifiers are facultatively aerobes, i.e., they are able to grow on oxygen and, alternatively, nitrate and nitrite when oxygen becomes limiting. Denitrifiers are very common, being found in soils, groundwater, sediments, and wastewater treatment plants.

Because denitrification reduces the nitrogen species, it requires an electron-donor substrate, which can be an organic compound or an inorganic compound. A very large range of biodegradable organic molecules can be the electron donor for the heterotrophic denitrifiers. Among the possible inorganic electron donors, H_2 and elemental sulfur (S^o) are the most important ones for the autotrophic denitrifiers.

In drinking water, electron-donor substrates always are too low to drive denitrification, and it is necessary to add a supplemental donor substrate. The supplemental donor plays two roles. First, it is utilized by heterotrophic bacteria to consume oxygen and create an anoxic environment conducive to denitrification. Second, it provides the electrons and energy to drive the sequential denitrification reactions. Having too little electron donor results in partial denitrification and the accumulation of NO_2^- or N_2O (Tiedje, 1988; Hamon and Fustec, 1991; Bernet et al., 1995; Wilderer, 1987; Schulthess et al., 1994, 1995, 1996).
Oxygen is the major regulator for denitrification activity (Kröger and Winkler, 1981; Körner and Zumft, 1989; Thomas et al., 1994; Rittmann and Langeland, 1985; Simpkin and Boyle, 1988; Lie and Welander, 1994; Schulthess et al., 1994) and controls denitrification at two levels: repression of enzyme synthesis and inhibition of enzyme activity. Generally, synthesis of denitrifying enzymes is permitted at higher oxygen concentrations than the threshold for activity of these enzymes. This situation allows the bacteria to be prepared for immediate use of nitrate when the O_2 concentration declines. For example, Körner and Zumft (1989) showed that the critical region for expressing nitrate reductase is <5.1 O_2/L for *Pseudomonas stutzeri* growing on nitrate, and O_2 concentration at 0.6mg/L or lower gave the maximum enzyme expression. Tiedje (1988) reported that the approximate inhibitory range of O_2 concentration for nitrate-reductase activity is 0.28-0.42mg O_2/L, while the threshold O_2 concentration for whole cells was found to be around 0.2-0.3mg/L (Rittmann and Langeland, 1985; Tiedje, 1988). In summary, denitrification is slowed through inhibition by an O_2 concentration greater than about 0.2-0.4mg/L, but denitrification is completely repressed (i.e., no reductase enzyme expressed) when the O_2 concentration is greater than about 5mg/L.

Although the optimum pH for denitrification appears to be 7 to 8 (Knowles, 1982; Thomas et al., 1994; Almeida et al., 1995b), it is not highly sensitive to pH and can occur at a pH as high as 11 (Prakasam and Loehr, 1972). pH outside of the optimum range

may cause accumulation of intermediates. Generally, nitrite is accumulated at alkaline pH, while nitrous oxide is accumulated at acidic pH (Thomas et al., 1994; Thomsen et al., 1994; Bernet et al., 1995). Denitrification consumes acid and may cause the pH to rise.

The rate of denitrification increases as temperature increases up to around 60 to 75°C (Knowles, 1982). Rate coefficients generally follow the Arrhenius relationship and roughly double with each 10°C increase in temperature (Lewandowski, 1982).

Experiences with Denitrification of Drinking Water

As is true for most of biological drinking-water treatment (Rittmann and Huck, 1989; Rittmann, 1995; Bouwer and Crowe, 1988), almost all denitrification processes employ a biofilm system as the strategy for biomass retention. Biofilm processes offer many powerful advantages for drinking-water treatment over a suspended-growth system. The most important advantage is the naturally occurring good cell retention by having high-density cell accumulation onto a large surface. This is a particularly beneficial situation when the substrate concentration is low, which is especially true for drinking water applications. Excellent cell retention by attachment also is very advantageous for slow-growing bacteria, such as autotrophs. Good cell retention also increases the removal capacity per unit volume of reactor and makes the process economical. Finally, excellent cell retention minimizes the amount of biomass that leaves the biofilm system with the treated water.

Heterotrophic denitrification has been the most common strategy for drinking water denitrification, primarily because of its wide and successful use in wastewater denitrification. Full-scale and pilot processes have used ethanol, acetate, or methanol as the electron-donor supplement (Richard, 1989; Mateju et al., 1992; Urbain et al., 1996; Philipot et al., 1985; Frick and Richard, 1985; Hiscock et al., 1991; Roennefahrt, 1985, 1986; Liessens et al., 1993; Green et al., 1994). Fixed beds of expanded clay or Styrofoam and fluidized beds of sand or sludge granules were used successfully to bring NO_3^--N levels below the 10mgN/L standard. Substrate loadings were quite high (up to 4,000gN/m^3-day), which gave small detention times, generally less than 15 minutes. These high loading operations gave significant concentrations of biodegradable organic matter in the effluent, and this required post-treatment efforts to produce a biologically stable water.

Autotrophic denitrification is not as well studied, but a significant body of information is gathering for *autotrophic denitrification* using H_2 as the electron donor, a process called *autohydrogenotrophic denitrification*. Autohydrogenotrophic denitrification offers two major advantages over heterotrophic denitrification:

1) It is impossible to have a residual of the supplemented donor, since H_2 evolves to the atmosphere once the water is expressed to an open surface; and

2) H_2 costs 3 to 15 times less than the common organic supplements to remove the same amount of NO_3^-. The main drawback to H_2 has been the risk of creating an explosive

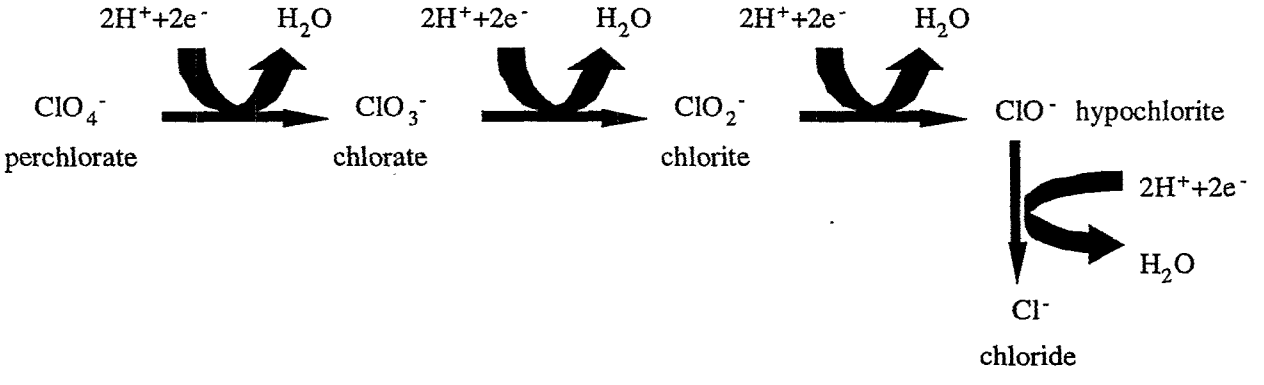
atmosphere. However, H_2 feeding through a bubbleless membrane device eliminates the risk.

Pilot-scale and commercial-scale studies used fixed-bed and fluidized-bed biofilm processes for autohydrogenotrophic denitrification and showed the ability to drive NO_3^--N concentration to levels below 0.1mgN/L, if desired (Tuisel et al., 1989; Dries et al., 1988; Gros et al., 1988; Kurt et al., 1987). NO_3^--N elimination rates were up to 550gN/m^3-day, giving liquid retention times less than 1 hour. All these processes used H_2 sparging, which limited the H_2 transfer rate.

Supported by a Small Business Administration grant and working cooperatively with Dr. Rittmann, Membran Corporation conducted a preliminary study using an upflow, fixed-bed biofilm reactor to investigate the feasibility of denitrification with bubbleless H_2. The biofilm in the reactor was colonized on Jaeger Tri-Packs® No. ½ (nominal size 1 inch). The hydrogen supply was provided through a Membran Bubbleless Membrane Gas-transfer system, which is essentially a bundle of hollow, gas-permeable membrane fibers enclosed in a standard water pipe. The denitrifying system was first operated to provide a steady-state biofilm with an approximate thickness of 1mm. Then, series of nonsteady-state, short-term experiments (20-30 min) were conducted by varying feed NO_3^- concentration ranging from 6.3 to 150mgN/L. The Membran study showed that they could produce an effluent with an N concentration below 0.1mg/L when the reactor H_2 concentration was high (>0.2mg/L), but that partial removal of NO_3^- was possible when the H_2 concentration was driven below approximately 0.16mg/L (H_2 as the limiting substrate). Therefore, hydrogen consumption was minimized by keeping hydrogen as the limiting substrate, while attaining nitrate concentration at a regulatorily acceptable level.

Fate of Perchlorate

When denitrifying bacteria are active and the concentration of NO_3^- is not too high, perchlorate (ClO_4^-) appears to be reduced though the action of nitrate reductase (Malmqvist et al., 1991). Sequential reductions ultimately lead to complete reduction to chloride ion:



The presence of a high concentration of NO_3^- stops perchlorate reduction (Malmqvist et al, 1991) and the likely cause for this is that NO_3^- outcompetes perchlorate for the nitrate

reductase. A high oxygen concentration also stops perchlorate reduction by repressing or inhibiting the nitrate reductase. Therefore, perchlorate reduction probably requires very low concentrations of NO_3^- and O_2.

Work by several groups shows that reduction of perchlorate or chlorate leads to energy conservation and biomass growth (Malmqvist et al, 1991, Malmqvist et al., 1992, US Patent 5,302,285). This reinforces the conclusion that ClO_4^- (or ClO_3^-) is replacing NO_3^- as the electron acceptor reacting with the nitrate reductase. It also means that perchlorate respiration can lead to selection and growth of perchlorate reducers (US Patent 5,302,285). In the drinking-water situation, however, perchlorate concentrations will be very low; hence, it is most likely that the bacteria carrying out perchlorate reduction gain most of their energy and growth through reduction of NO_3^-, not ClO_4^-.

Table 2-1 lists the expected stoichiometry for perchlorate reduction (to Cl^-) with acetate, methanol, and H_2 as the supplemental electron donor. The stoichiometry was estimated using the thermodynamic method of McCarty (1972). In all cases, ClO_4^- is a highly energetic electron acceptor, which makes biomass yields and specific growth rates relatively large. For H_2, the carbon source is inorganic carbon, which normally is amply available from the water's bicarbonate alkalinity. The heterotrophic bacteria growing with methanol, a one-carbon molecule, are distinctly different species from those grown on acetate and other common organic molecules that have two or more carbons. interesting

Table 2-1
Estimated Stoichiometries for Biomass Synthesis and Perchlorate Respiration-with Acetate, Methanol, and H_2 as the Electron Donor

good

Acetate
Reaction:
$$0.125CH_3COO^- + 0.098ClO_4^- + 0.008NO_3^- + 0.008H^+ \equiv 0.008C_5H_7O_2N + 0.098Cl^- + 0.125HCO_3^- + 0.086CO_2 + 0.101H_2O$$
Observed Yield: 0.11 gVSS/gO.D.=0.11 gVSS/g acetate

Methanol
Reaction:
$$0.167CH_3OH + 0.093ClO_4^- + 0.009NO_3^- + 0.009H^+ \equiv 0.009C_5H_7O_2N + 0.093Cl^- + 0.122CO_2 + + 0.306H_2O$$
Observed Yield: 0.13 gVSS/g O.D.=0.19gVSS/g methanol

Hydrogen
Reaction:
$$0.5H_2 + 0.119ClO_4^- + 0.002NO_3^- + 0.009CO_2 + 0.002H^+ \equiv 0.002C_5H_7O_2N + 0.119Cl^- + 0.495H_2O$$
Observed Yield: 0.028 gVSS/g O.D.=0.20 gVSS/g H_2

Stoichiometry and observed yields are computed based on the thermodynamic method (McCarty, 1972) and with a decay rate of b = 0.15/d, a biodegradable fraction of f_d = 0.8, and a solids retention time of θ_x=15 days. O.D. refers to oxygen demand of the electron donor.

Table 2-2 lists the required amounts of acetate, methanol, and H_2 needed to remove one gram of NO_3^--N, ClO_4^-, and O_2. If a water contains 15mg/L NO_3^--N, 1mg/L ClO_4^-, and 2mg/L O_2, the required supplements of acetate, methanol, and H_2 would be 14, 10, and 1.5 mg/L, respectively. Designing a biofilm process with an acetate volumetric loading of 5,000g/m^3-day (a typical value used successfully for denitrification) gives a hydraulic detention time of 4 minutes. Thus, design of a denitrification process to remove perchlorate as well appears to be feasible.

Table 2-2
Grams of Acetate, Methanol, and H_2
Needed to Remove One Gram of the Three Main Electron Acceptors

	Electron Donor		
Electron Acceptor	Acetate	Methanol	H_2
NO_3^--N	0.71	0.53	0.083
ClO_4^-	0.76	0.58	0.085
O_2	1.2	0.88	0.13

Stoichiometries are determined in the same way as for Table 2-1.

Well written

QUESTIONS

Although perchlorate reduction coincident with denitrification appears to be feasible in the drinking-water setting, major questions must be answered before it is ready for pilot testing.

1. Do the bacteria that accumulate during drinking-water denitrification carry out perchlorate reduction? If the answer is yes, we can proceed directly to the next questions. If the answer is no, then we must ascertain the cause: e.g., lack of a key nutrient, use of a supplemental electron donor that selects for denitrifiers that do not reduce perchlorate.

2. Will biological treatment be effective for waters containing perchlorate at µg/L levels with no significant nitrate concentration present? In other words, if no nitrate were present, would the very low levels of perchlorate - less than 100 µg/L - select for bacteria that can reduce perchlorate)?

3. What is the rate-limiting mechanism for perchlorate reduction and what are the kinetics for that mechanism? Possible limiting mechanisms are competition from NO_3^-, reduction kinetics for ClO_4^-, or oxidation kinetics for the donor.

4. What is the "best" supplemental electron donor? Organic electron donors have been widely studied and give reliable denitrification. However, they have real drawbacks: high cost, residual biological instability, and acute health risks (from methanol). For methanol (or ethanol), a license for its use must be obtained from the Department of Alcohol, Tobacco, and Firearms (ATF). H_2 gas overcomes all

those drawbacks, but has been much less studied and must be applied in a way that minimizes the risk of explosion.

5. What will be the effluent quality? Particular issues are intermediate byproducts - such as chlorate and chlorite - nitrite, biological stability, disinfection by-products, and microorganisms.

6. What are the post-treatment needs to make the effluent potable?

7. What are the fates of possible co-contaminants, such as the chlorinated solvents?

8. What is the engineering and economic feasibility for making biological perchlorate reduction a reliable process?

RELEVANT RESEARCH BY THE PARTNERS

The research partners – Northwestern University and Montgomery Watson – have recent and ongoing experiences that make us especially capable of performing research on biological perchlorate reduction.

Currently, Dr. Rittmann is directing a research study on autohydrogenotrophic denitrification of drinking water using bubbleless gas transfer. We have a novel membrane biofilm reactor, shown in **Figure 2-1**, that achieves denitrification that can be carefully controlled by adjusting the H_2 pressure to the Membran Corp.'s patented membrane module, which also is the biofilm support medium. Under routine operating conditions, we can reduce NO_3^- from 15mgN/L to 0.1mgN/L with a hydraulic detention time of 2 hours or less. Partial NO_3^--N removal to meet regulatory standards is attained with shorter detention times or by reducing the H_2 pressure.

As part of our preparation for this proposal, we challenged this system for eight hours with a feed of 1.1 mg/L of ClO_4^-, and the system reduced perchlorate to 0.6 mg/L under the routine operating conditions and without any time allowed for acclimation of the bacteria to perchlorate. This finding strongly supports our hypothesis that perchlorate reduction is widespread among denitrifiers, particularly among H_2-oxidizing autotrophs. It underlines the great potential of using H_2 as the electron donor supplement.

Over the past decade, Dr. Rittmann's group has developed small-scale biofilm reactors for the investigation of degradation kinetics with biofilms. These completely mixed biofilm reactor systems, illustrated in **Figure 2-2**, are ideal for mechanistic and kinetic analyses, because inputs can be carefully controlled, liquid concentration are nearly uniform, and mass-transport is well-defined. They have been used to determine kinetics for oligotrophic systems of direct relevance to drinking water (Rittmann et al., 1986; Rittmann and Manem, 1992). Of great significance to the study here is the adaptation of our completely mixed biofilm reactors to study strictly anaerobic systems in which O_2 must be excluded (Wrenn and Rittmann, 1996; Raskin et al., 1996).

Montgomery Watson is an environmental engineering firm with corporate headquarters located in Pasadena, California. Although it does business in all aspects of environmental engineering, the firm is most known for its strength in water treatment. Specifically, Montgomery Watson's Applied Research Department has been conducting water treatment bench- and pilot-scale studies for water utilities across the United States for the past 12 years.

Montgomery Watson's Applied Research Department is currently conducting a treatability study on the removal of perchlorate from groundwater using ion-exchange. The project involves pilot scale testing of the process including the application of biological treatment for the removal of the concentrated perchlorate from the spent regeneration brine solution.

PROJECT APPROACH

Overview

The proposed research is designed to answer the critical questions through bench-scale experiments and engineering analysis. The bench-scale studies will be conducted at Northwestern University. Steady-state screening experiments will be used to select the optimal organic electron-donor (acetate or methanol) and to ascertain if H_2 is a feasible electron donor. Then, in-depth bench-scale studies will identify the rate-limiting mechanism for perchlorate reduction and the kinetics that describe that mechanism. The optimal organic electron donor and H_2 (if shown feasible) will be evaluated in detail. Throughout the screening and in-depth studies, the effluent quality will be evaluated. Towards the end of the in-depth studies, the biofilm systems will be challenged with chlorinated solvents.

The fundamental and engineering work performed here will lead directly to a Phase II study on integrating denitrification with post-treatment, scale-up, operability, and costs assessments. Montgomery Watson will carry out the works to assess engineering feasibility and design a Phase II plan.

Below we describe the objectives and the methods for the 11 tasks that comprise the research plan. The timing for the for the tasks is outlined in Section 5: Schedule.

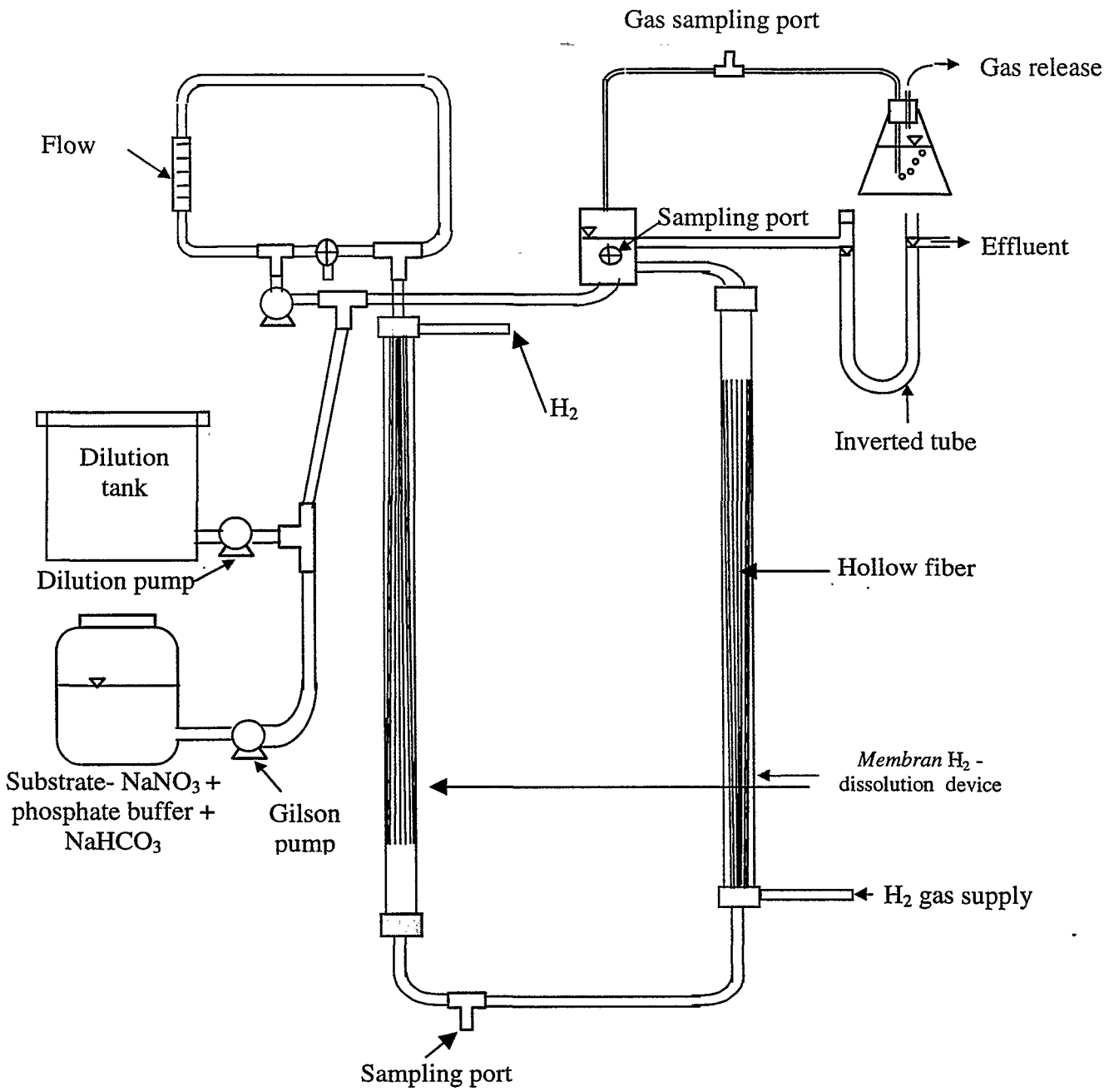


Figure 2-1.
Schematic of the membrane biofilm reactor used currently by Northwestern University to denitrify drinking water.

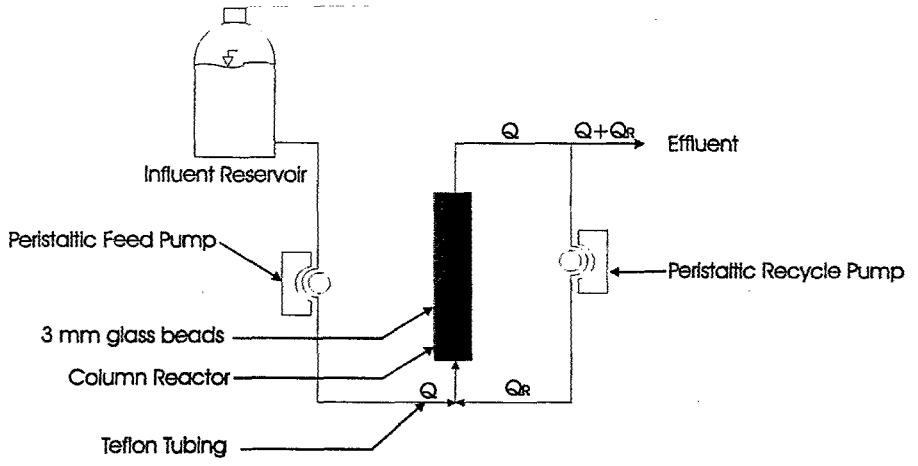


Figure 2-2
Schematic of the completely mixed biofilm reactor system used for mechanistic and kinetic analysis

Drawback

Task 1: Construct Systems

The objective of this task is to design and construct the reactors that will be used for the experiments described in tasks 4 to 8. Three completely mixed biofilm reactors will be required for the experiments:

a) Two porous medium reactors, one each for acetate and methanol; and
b) One membrane biofilm reactor for H_2

The two porous medium biofilm reactors (item a) will be constructed following the schematic drawing provided in **Figure 2-2**. **Table 2-2** lists physical parameters of the systems as they have been used in the past. Since the reactors will be run under anoxic conditions, measures will be taken to ensure O_2 is excluded. The most important such precaution is minimizing oxygen transfer through the reactor tubing, which will be achieved by using the most oxygen-impermeable tubing available: flexible PVC tubing for the feed pump, Norprene in the recycle pump, and teflon encased in Norprene for the transfer tubing (Wrenn and Rittmann, 1996). In addition, the feed medium will be deoxygenated and kept under N_2 atmosphere (Wrenn and Rittmann, 1996). A second precaution is release of gases from the porous medium reactor, since significant N_2 formation will occur. We will install a degassing chamber in the recycle line to minimize the recycle of supersaturated N_2. **Figure 2-1** shows such a degassing chamber in our membrane biofilm reactor. We also will install syringe ports along the reactor for manual removal of trapped gas, a method we used successfully in the past (Rittmann et al., 1988).

The hydrogen membrane biofilm reactor (item b) already is built and is currently in use at Northwestern University. A schematic of the reactor is provided in **Figure 2-1**. The reactor will be available for use in this project; therefore, no new bench scale reactor for H_2 will need to be constructed.

For the estimation of kinetic parameters, both systems create the biofilm analog of a continuously stirred tank reactor (CSTR), which greatly simplifies estimation of the parameters describing substrate utilization: q_m and K for Monod relationship, $r_{ut}= -q_m SX/(K+S)$.

Table 2-3
Characteristics of Completely Mixed Porous Media Biofilm Reactors

Parameter	Measurement
Length of reactor	21.5 cm
Diameter of reactor	2.5 cm
Cross sectional area reactor, A_{cs}	4.91 cm^2
Volume of reactor, V	105.5 cm^3
Diameter of glass beads, D_p	0.3 cm
Area of glass bead, A	0.282 cm^2
Specific surface area, a	12.0 cm^{-1}
Porosity, $\gamma=V_v/V$	0.4
Volume of voids, V_v	42.2 cm^3
Feed flow rate, Q	125.0 cm^3/h*
Detention time, 2= V_v/Q	20.3 min*
Recycle ratio, Q_R/Q	20*
Time of one pass through column, $V_v/(Q+Q_R)$	0.96 min*
Superficial velocity of fluid	8.91* cm/min

*All of these parameters are easily varied to control loadings and mixing.

Kinetic experiments involve challenging the reactors with a wide range of influent concentrations of perchlorate, nitrate, or the electron donor. Once steady state is reached (typically 2 to 6 hours), the effluent concentration is obtained. For all substrates except H_2, the substrate flux (J) is computed from

$$J = Q\frac{(S_o - S_e)}{A} \qquad (1)$$

in which S_o is the influent concentration and S_e is the effluent concentration. The log-mean concentration of substrate (S_m) is used as an estimator of the average concentration in the completely mixed biofilm reactor.

$$S_m = \frac{(S_o - S_e)}{\ln(S_o/S_e)} \qquad (2)$$

A curve-matching technique (Rittmann et al., 1986) is then used to estimate K and the product $q_m X_a$. Separate measurements of the biofilm density (X_a) allow an independent measure of q_m (Rittmann et al., 1986). For H_2, its flux must be determined from the measured flux of perchlorate and/or nitrate and a stoichiometric conversion, as illustrated in **Table 2-2**. We have used this stoichiometric method successfully in our research on autohydrogenotrophic denitrification.

Task 2: Analytical Methods

The following are the principal analytical methods to be used in the research.

- **Dissolved oxygen**. Dissolved oxygen is measured by a Clarke-type polarigraphic probe (Orion Dissolved Oxygen/BOD Probe).

- **Perchlorate**. Perchlorate is measured using ion chromatography methods following modified EPA 300.0. The water sample is injected into a stream of sodium hydroxide eluent with p-cyanophenol as a modifier and passed through an ion exchange resin for separation based on relative resin affinities. The separated ions are then carried through an anion micromembrane suppressor and converted to their highly conductive acid form, $HClO_4$. The separated ions in their acid form are measured by conductivity, and anions are identified based on their retention time compared to standards.

- **Chlorate, Chlorite, and Chloride.** Chlorate and Chlorite are measured by an ion exchange chromatography method. Chloride ion will is measured using the Argentometric method, following APHA, 1989 Method 5530 D.

- **Trihalomethane formation potential (THMFP).** THMFP will be determined following method 5710B of *Standard Methods.*

- **Nitrate and Nitrite**. NO_2^--N is measurd by the diazotization method (Standard Mehtod 4500- NO_2 B). This colorimetric method is suitable for concentrations of 0.005 to 1 mg NO_2^--N/l. After the NO_2^- concentration is determined, NO_3^- is reduced to NO_2^- by the cadmium reduction method (Hach method) and measured as total nitrogen concentration minus the NO_2^--N concentration. Proper dilutions may be required when the concentration exceeds the limit of the test range (0.1 to 4.5 mg NO_3^--N /l).

- **Hydrogen**. The H_2 (g) is analyzed by a Trace Analytical RGA3 reduction gas analyzer, in which H_2 directed through HgO produces Hg(g), which is measured by an ultraviolet photometer. For the dissolved-phase H_2 measurement, head-space analysis is used. 1 ml of liquid sample from the reactor is quickly transferred to a 160-ml serum vial previously outgassed with hydrogen-free nitrogen. The vial is then shaken vigorously to liberate the dissolved H_2. A gas-tight syringe is used to take the head-space sample (1 ml) and test for the H_2 concentration. Once the H_2 concentration is known, the dissolved H_2 concentration can be determined by Henry's law and mass balance.

- **VOC's**. TCE and PCE are VOCs of interest to this study. They can be measured in a gas chromatograph with electron capture detector, such as a Hewlett-Packard HP-5890. The target VOCs are separated on a 6' x ¼" glass column packed with 80/100 Carbopack B coated with 1% SP-1000. The column is operated at 190°C, and the injector port and detector temperatures are 230 °C. The carrier gas is 5% methane in

argon, and the flow rate is 30 ml/min. Specific retention times for TCE and PCE can be determined for these conditions.

- **TOC/DOC.** The TOC/DOC will be assayed with a Dohrmann/Rosemount DC-180 low-level analyzer. The DOC is obtained after filtration with a 0.45-μm membrane filter that has been thoroughly rinsed with distilled water. Biomass is measured as the filterable (or suspended) TOC. Since the TOC analyzer can also measure total carbon (TC), the inorganic carbon can be measured as the difference between TC and TOC.

- **Biodegradable Dissolved Organic Carbon (BDOC).** BDOC type tests are a surrogate to estimate the Biodegradable Organic Matter (BOM). BDOC tests equate BOM to the decrease in dissolved organic carbon (DOC). We will use the method of Joret et al. (1991), who employs a high-density inoculum of organisms attached to sand obtained from a biologically active drinking water filter. The sand inoculum is first washed until DOC in the wash water is no longer detectable. Then, 100 g of sand is combined with unfiltered water and incubated at room temperature until no further change in DOC level is detected. The BDOC is equal to the change in DOC.

Task 3: Continuous Literature Evaluation

An extensive literature review for autotrophic dehydrogenation has already has been performed at Northwestern University (Appendix B). We also reviewed the limited information currently available on perchlorate removal by biological methods. Literature will be continuously reviewed throughout the duration of the project to collect any new information. The latest update of the literature review will be included with the final report.

Task 4: Steady-State Screening Experiments

Initial screening studies will be conducted to ascertain if H_2 is a viable electron donor for perchlorate reduction and to determine if acetate can be used in lieu of methanol as an organic electron donor. Our preliminary perchlorate challenge suggests that H_2-oxidizing autotrophs will perform perchlorate reduction, but a much more comprehensive evaluation is needed. We would prefer to utilize acetate over methanol, since methanol is acutely toxic to humans and is regulated by the ATF. However, acetate should not be chosen if it is inferior in terms of perchlorate reduction or costs.

For the initial screening runs, we will operate the three completely mixed biofilm reactors in parallel. The feed will be mineral medium supplemented, as needed, with ClO_4^-, NO_3^-, and organic electron donor. Once steady state is achieved, we will measure removal of perchlorate, formation of perchlorate intermediates, and release of biodegradable dissolved organic carbon. If the H_2 system provides reasonable performance, we will move ahead to the next phase with it. If perchlorate removal is minimal or intermediates formation is substantial, we will stop work on H_2. We will select acetate for further studies with heterotrophic denitrification unless acetate gives poor perchlorate removal, excessive intermediates formation, or economics unfavorable compared to methanol.

Task 5: Reaction Mechanisms

Reaction mechanisms will be explored by operating the bench-scale reactors for different combinations of electron donors and acceptors. Scenarios will be performed for H_2 and the optimal organic donor (acetate or methane) and will explore the following:

- **Inhibition by NO_3^-.** We suspect that NO_3^- and ClO_4^- compete for the nitrate-reductase enzyme. Therefore, a high concentration of NO_3^- should inhibit ClO_4^- reduction. We will vary the NO_3^-: ClO_4^- ratio in the reactor to observe this effect.

- **Inhibition by O_2.** O_2 concentrations greater than a few tenths of a mg/L inhibit nitrate reduction by nitrate reductase. We anticipate that ClO_4^- reduction also will be inhibited. We will expose the systems to several mg/L O_2 (by oxygenating the feed solution) to observe the control exerted by O_2.

- **Effects of pH.** By using buffers, we will alter the pH from its normal value (approximately 7.5) to evaluate the short-term effects of pHs not near neutral. Higher pH values, caused by base generation from denitrification, are of the greater interest.

- **Formation of Soluble Microbial Products.** All microorganisms release dissolved organic molecules known as soluble microbial products (SMP) (Namkung and Rittmann, 1986; Noguera et al., 1994; Rittmann et al., 1994). In most microbiological processes, SMP comprises the large majority of the effluent DOC. For drinking water, it probably is the majority of the BDOC. We will assay DOC and BDOC concentrations to determine the impact of SMP on effluent quality and biological stability.

- **Formation of Intermediates.** Ideally, ClO_4^- is reduced to Cl^-. However, an indequate supply of electron donor, competition with NO_3^-, or slow kinetics may cause an accumulation of perchlorate intermediates, such as chlorate or chlorite. We will vary the supply rate of the supplemental electron donor, as will as NO_3^- and O_2, to evaluate conditions that lead to accumulation of intermediates.

- **No Nitrate.** If the water contains low concentration of ClO4- and no nitrate, we will determine if the presence of only ClO4- selects for bacteria able to reduce chlorate. The depletion of dissolved oxygen should be a controlling factor, and we will test conditions in which the electron donor does or does not deplete the dissolved oxygen.

The results of these experiments will confirm the mechanism(s) that govern perchlorate reduction and effluent quality in biofilm treatment for perchlorate reduction. These parameters will be those that subsequently must be considered for engineering design of pilot-scale or full-scale reactors.

Task 6: Kinetics of Rate-Limiting Mechanisms

Once the controlling mechanism(s) is (are) known, we will conduct experiments to determine the kinetics of perchlorate removal. Although the details of the kinetic experiments cannot be laid out before the controlling mechanism is known, the general strategy can be outlined. For instance, the rate-limiting substrate could be the electron donor, ClO_4^-, or NO_3^- (as an inhibitor). If the donor is rate limiting, its concentration will be varied systematically by controlling its supplementation rate. Thus, the fluxes of the donor and ClO_4^- (recall eqn. 1) are computed. These rates are then combined with the log-mean concentrations of the donor (and estimated parameters for mass transport) to determine the Monod kinetic parameters q_m and K. This proven technique (Rittmann et al., 1986) can be used directly when acetate, methanol, or perchlorate is limiting. When H_2 or NO_3^- is limiting, the technique to extract the parameters will need to be altered from the curve-matching approach. Nonlinear fitting using a reaction-with-diffusion model is needed. This approach already is developed for H_2 limitation as part of our ongoing project on autohydrogenotrophic denitrification. It will be extended for NO_3^- inhibition if needed.

Task 7: VOC challenge

Since VOC co-contaminants may be present under actual treatment conditions, the bench-scale reactors will be challenged with PCE and TCE to determine their fate and impact on treatment efficiency. For perchlorate, reductive dehalogenation (biological transformations of VOCs into less halogenated compounds) is a likely fate and will be monitored by gas chromatography. The VOCs might compete with perchlorate as an electron acceptor, and VOCs might reduce perchlorate removal rates.

Task 8: Effluent Quality

Effluent quality will be monitored throughout tasks 5, 6, and 7. Parameters will include BDOC and DOC (mainly from SMP), intermediates of perchlorate reduction, NO_2^-, and trihalomethane formation potential.

Task 9: Conduct Engineering & Economic Analysis

The objective of this task is to assess the engineering and economic feasibility of the biological treatment project. The bench-scale testing will provide a wealth of information on the reaction rates, substrate requirements, and other fundamental data on the performance of the biological process for perchlorate reduction. In this task, Montgomery Watson will conduct a thorough engineering and economic analysis of the application of this process for the removal of perchlorate from contaminated drinking water. The analysis will be conducted based on the water quality and site-limitations of each of the three participating utilities on the project. The analysis will include an evaluation of the following issues:

1. Post treatment requirements for application as a drinking water treatment process

2. Scale-up of process parameters to the large-scale applications of municipal drinking water
3. Operability and reliability of the process
4. Capital and O&M costs of the process
5. Development of the process flow diagram and design criteria

The engineering and economic analysis will be included in the project final report and will provide the foundation for determining whether this process can be reliably and cost-effectively implemented as a water treatment process.

Task 10: Develop Phase II Testing Plan

The objective of this task is to develop a proposed pilot testing plan for Phase II. Phase I of this project focuses on conducting bench-scale evaluation of the biodegradation of perchlorate in contaminated drinking water. AWWARF has a preliminary plan to continue with Phase II of the project by focusing on pilot-scale testing and demonstration of the process under field conditions. We propose that, as part of the final report for Phase I, we develop a proposed testing plan for Phase II. If our project team is selected to continue with Phase II activities, then this plan will be used as a nucleus for the overall scope of work under Phase II. Since the final report of Phase I will undergo the PAC review process, then the testing plan in the final report will include all the comments of the PAC and will therefore be ready for implementation in Phase II.

Task 11: Write Progress Reports and Final Report

As per AWWARF guidelines, we will submit progress reports each four months and the draft final report about one month before the end of the project.

SECTION 3
APPLICATIONS POTENTIAL

It is true that the perchlorate contamination problem has so far been limited to California, Nevada, and one well in Utah. However, perchlorate has long been used as a solid-rocket fuel. Facilities that manufacture(d) , use(d), or handle(d) solid rocket fuel (for rockets, munitions, or fireworks) are scattered across the United States. The sister AWWARF project evaluating the national occurrence of perchlorate may determine that the contamination problem is more wide-spread than currently perceived. Considering that little to no information is available on the removal of perchlorate by water treatment processes, it is imperative that research be conducted to assess the feasibility and cost of removing perchlorate from contaminated drinking water. This project, and the accompanying projects funded by AWWARF, will develop a sufficient treatment database that will allow any water utility with a perchlorate contamination problem to immediately determine what they need to do to solve their problem.

In addition, this project has direct relevance to the application of biological treatment for the removal of nitrate from contaminated groundwater. For a long time, biological denitrification has long been used in wastewater treatment, but not in drinking water treatment. Due to concerns about operating a biological process in a water treatment plant, nitrate removal in the United States has been largely limited to ion-exchange or membranes, both of which are expensive processes. The results obtained in this study, which will look at simultaneous biological perchlorate removal and denitrification, will indirectly evaluate the design and operational issues related to a biological drinking water denitrification process.

SECTION 4
QUALITY ASSURANCE/QUALITY CONTROL

Quality Assurance

Wherever possible, methods have been selected *from Standard Methods for the Examination of Water and Wastewater*, 19th edition (APHA, 1997). All methods will employ strict Quality Assurance/Quality Control (QA/QC) procedures. Personnel of the Research team have expensive experience with the analytical methods described below.

Reagents, Glassware For Analyses And Water Sample Collection

Water for the preparation of all solutions will be ultra-pure water produced by Milli Q-UV Plus systems (Millipore Corp.). Laboratory reagents will be obtained at a greater than 98 % purity and will be used as received.

All the glassware will be cleaned in a stainless steel dishwasher employing a detergent wash, an acid wash, and distilled water rinses. The glassware will be muffled at 550 °C for 4 hours to remove any organic contamination.

When analyses cannot be performed on-site, samples will be immediately placed on ice for transport and stored in a refrigerated state until assays are performed.

Standard QA/QC Procedures

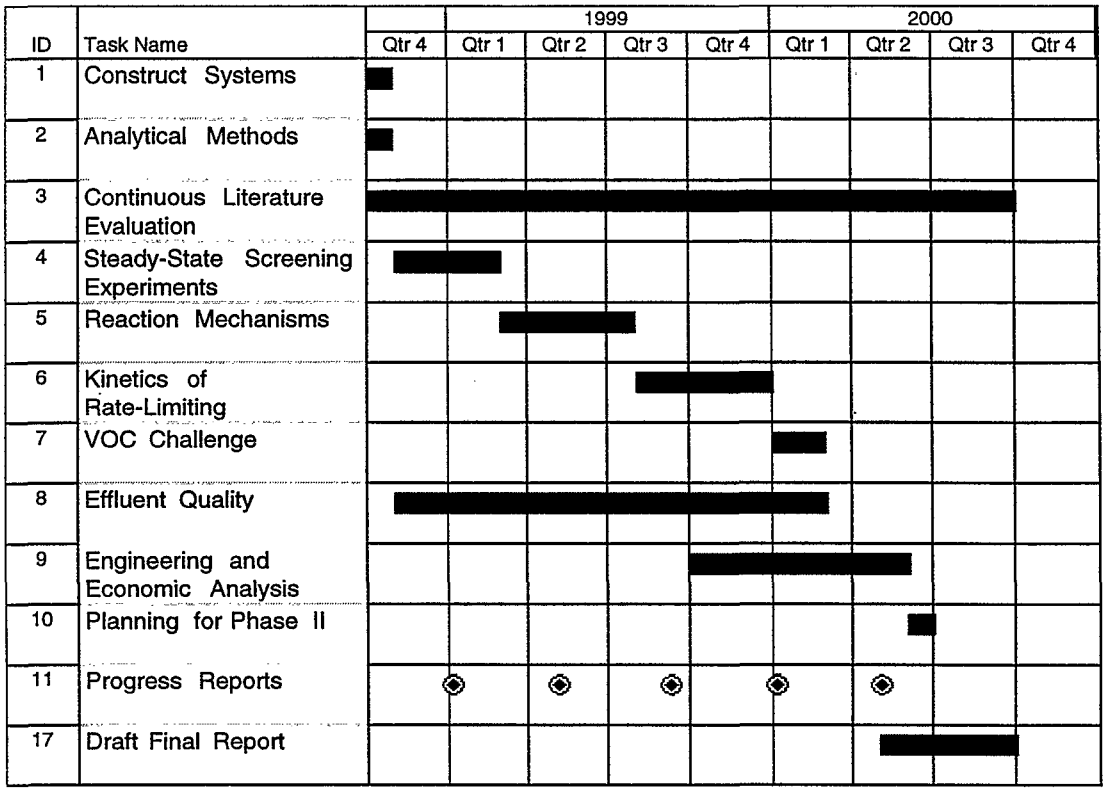
Standard laboratory practices such as positive and negative controls; sterility checks; daily recording of incubator, refrigerator and freezer temperatures; technician performance; laboratory pure water; and reagent purity will be followed as outlined in the 19th edition of *Standard Methods*, the EPA manual *Handbook for Certification of Bacteriological Laboratories*, or the relevant ASTM procedure. All QA/QC procedures will be documented and recorded in laboratory notebooks. The notebooks will be available for inspection.

Data Reduction, Reporting, Statistics

All data will be collected and stored electronically with backup copies made routinely. All hardcopies of original sample sheets will be stored as a reference. If appropriate, original data will be presented in appendixes of the final report. Statistical analyses will be performed using Statgraphics software on a PC computer.

SECTION 5
SCHEDULE

The project is broken into 11 tasks to be completed over 24 months, as indicated in the GANNT chart, below. The tasks were described in Section 2, subsection on Project Approach, pages 2-9 to 2-16.



SECTION 6
STATEMENT OF QUALIFICATIONS

OVERALL PROJECT TEAM

Our proposed project team includes Northwestern University's Environmental Engineering program (Professor Bruce Rittmann) and Montgomery Watson's Applied Research Department (Issam Najm). Professor Rittmann introduced the drinking water field to the idea of biological stability in 1984 (Rittmann and Snoeyink, 1984) and has been a leading researcher on biofilm treatment of drinking water from the initiation of the field until the present. His work at the University of Illinois, and now at Northwestern University, has focused on the application of biological processes for the de-contamination of drinking water. Issam Najm is the manager of Montgomery Watson's Applied Research Department located in Southern California. He has extensive experience with the testing and evaluation of physical, chemical, and biological water treatment processes. He brings strong familiarity with the perchlorate contamination issue in California and is currently conducting a perchlorate-treatability study for the Main San Gabriel Basin Watermaster. The project is evaluating the use of ion-exchange technology for perchlorate removal, coupled with biological treatment for the removal of perchlorate (and nitrate) from the brine solution.

Figure 6-1 shows a project organizational chart. Northwestern University will lead the project team during Phase I of the project, which addresses fundamental evaluation of the application of biological processes for perchlorate removal from drinking water. Montgomery Watson will provide technical support in the form of obtaining water quality information on the contaminated groundwater, conducting engineering and economic analysis of the process for pilot- and full-scale applications, and planning the Phase II activities. If our project team is selected to continue with Phase II, the project leadership will be reversed due to the practical nature of Phase II, which will include extensive field scale testing and demonstration of the process. We believe that our team brings an ideal mix of strong fundamental understanding of biological water treatment processes coupled with practical hands-on familiarity with the perchlorate contamination issue and water treatment engineering in general.

Three water utilities from Southern California and Nevada have committed to joining our team and participating in the project:

1. City of Riverside
2. Main San Gabriel Basin Watermaster
3. Southern Nevada Water Utility

These water agencies are substantially affected by the perchlorate contamination problem and are highly interested in evaluating perchlorate treatment options. During Phase I of the project, their role will include providing the project team with water quality information on their water sources, as well as providing review and comments on the project progress and findings. As part of the engineering and economic analysis to be conducted by Montgomery Watson, a conceptual process design will be developed for

each of the three utilities based on their specific water quality requirements (such as nitrate and perchlorate concentrations). In addition, as part of Phase I final report preparation, Montgomery Watson will develop the proposed pilot-scale testing program to be implemented in Phase II of the project, if it is awarded to our team. During Phase II of the project, the three participating utilities listed above will have priority for having the field demonstration testing conducted at their sites. The extent of their involvement and contribution to the project can only be determined at the conclusion of Phase I.

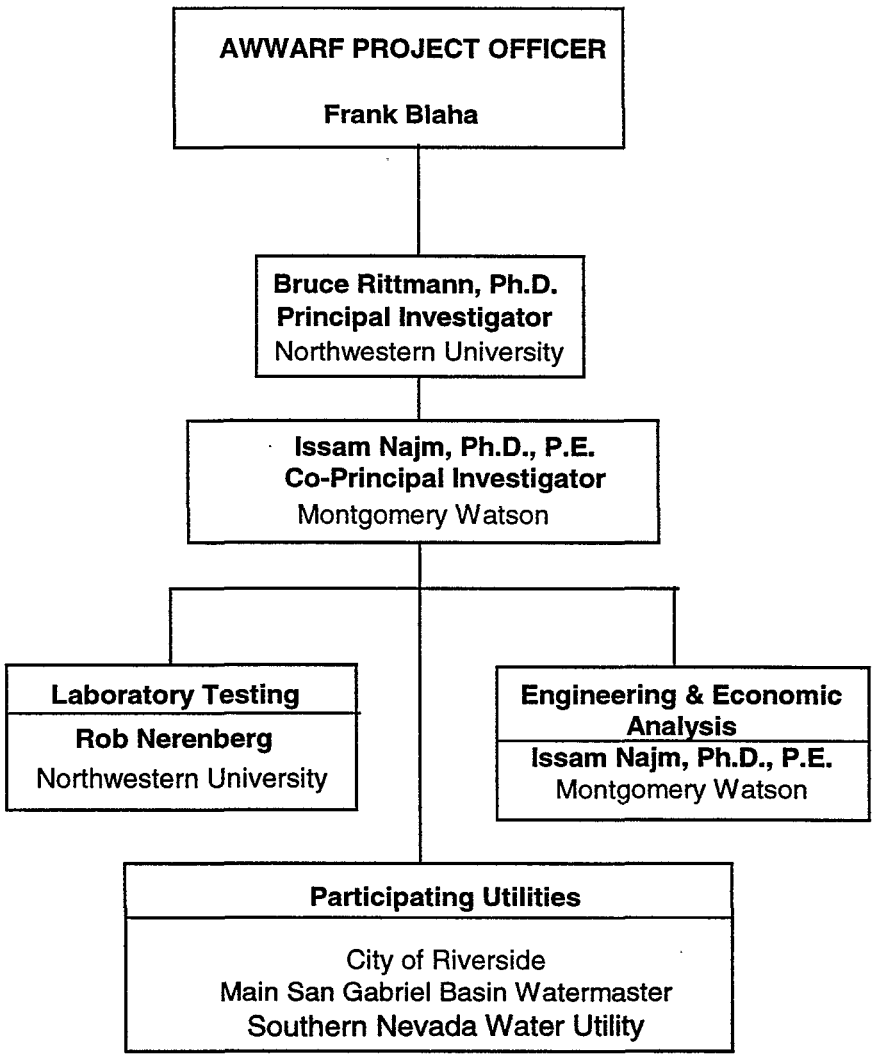


Figure 6-1
PROPOSED ORGANIZATIONAL CHART

The following is a brief description of the qualifications, roles, and responsibilities of each of the project team members. Detailed Resumes of the project team members are included in Appendix C.

STATEMENT OF QUALIFICATIONS

Bruce Rittmann, Ph.D. - Principal Investigator

Dr. Bruce Rittmann is John Evans Professor and Area Coordinator of Environmental Engineering at Northwestern University. His research combines concepts and techniques from engineering with those from microbiology, biochemistry, and microbial ecology. This combination is used to address fundamental and applied issues in the biological treatment of waters and wastewaters, as well as in the bioremediation of contaminated aquifers. Dr. Rittmann is most recognized for his research on biofilm kinetics, the biodegradation of organic and inorganic micropollutants, and the application of molecular and modeling tools to understand and control complex microbial systems used in environmental biotechnology. His work ranges from fundamental studies, such as on the genetics of nitrifying bacteria and the responses of intracellular cofactors, to applied studies, such as evaluating the performance of biofiltration systems used in drinking water treatment.

Dr. Rittmann served as the President of the Association of Environmental Engineering Professors and the Vice-Chair of the Water Science and Technology Board of the National Research Council (NRC). Dr. Rittmann was awarded the first A.R.I. Clarke Prize for Outstanding Achievements in Water Science and Technology from the National Water Research Institute (NWRI), and he previously won the Walter Huber Research Prize from the American Society of Civil Engineers (ASCE), the University Scholar Award from the University of Illinois, and the Presidential Young Investigator Award from the National Science Foundation. Dr. Rittmann is a fellow of the American Association of the Advancement of Sciences (AAAS).

Dr. Rittmann will serve as the principal investigator on the project and will be responsible for overall project direction and conduct. He will be responsible to AWWARF and the PAC for project progress and deliverables. He will design and supervise all project activities, including the development of the bench scale testing program at Northwestern University, as well as the analysis and interpretation of the project results. As such, Dr. Rittmann will commit approximately 9 percent of his time to the project.

Issam Najm, Ph.D., P.E. - Co-Principal Investigator

Dr. Najm is the manager of Montgomery Watson's Applied Research Department located in Pasadena, California. He has seven years experience in conducting and supervising bench-scale and pilot-scale water treatment studies for water utilities across North America. He commonly works with water utilities in addressing treatment process issues and developing means of resolving water quality problems. He is currently the principal investigator on two AWWARF funded projects: the first titled: "Case Studies of Impact of Treatment Changes on Biostability of Full-Scale Distribution Systems", and the second titled: "Bromate Formation and Control During Ozonation of Low-Bromide Waters." In addition, Dr. Najm is currently the project manager on a perchlorate treatment feasibility study funded by the Main San Gabriel Basin Watermaster in Southern California. The project includes bench-scale and pilot-scale testing of a conventional ion-exchange process for the removal of perchlorate from contaminated

groundwater. The project will also investigate the use of biological treatment for the removal of perchlorate (and nitrate) from the process regeneration brine.

Dr. Najm will serve as the co-principal investigator on the project during Phase I and principal investigator during Phase II (if selected by AWWARF for Phase II). He is very familiar with the perchlorate contamination issues in California and understands the engineering issues associated with groundwater treatment. His primary role on the project will be to conduct the engineering and economic analysis of the process, and develop a preliminary design criteria for the application of the process at the three participating utilities. As such, he will commit 8 percent of his time to the project.

Robert Nerenberg, P.E. - Laboratory Testing

The proposed research is experimentally intensive and will involve the full time participation of one graduate student, Robert Nerenberg. Mr. Nerenberg has his B.S. from the University of Buenos Aires, Argentina, and his M.S. degree from Wayne State University, Detroit. He has seven years of consulting experience in the environmental field, including 5 years with Harza Environmental Services, Inc. in Chicago. He is a registered Professional Engineer in Wisconsin. Currently, Mr. Nerenberg is pursuing the Ph.D. degree in environmental engineering at Northwestern University.

Mr. Nerenberg will work under the direction of Dr. Rittmann and will be responsible for the project's day-to-day activities. Such activities may include planning and coordination of experiments, operation of the bench scale plants, collection and analysis of samples, preparation of interim reports, and preparation of the final report. Mr. Nerenberg will also direct the activities of any undergraduate students employed as helpers. Mr. Nerenberg's technical and organizational skills gained through 7 years environmental consulting will help promote the project's successful and timely completion.

NORTHWESTERN UNIVERSITY

Northwestern University's Environmental Engineering Program has available our 5,000 sq. ft. of laboratory space devoted to research. This space was renovated to state-of-the-art in 1992. In addition to full capability for wet chemistry, the program houses all specialized equipment and facilities needed. These include the following:

- Walk-in temperature control chamber
- Anaerobic glove box
- Anaerobic gasing stations
- Autoclave
- Four gas chromatographs
- Hitachi HPLC System
- Dionix Ion Chromatograph
- Trace Analytic RGA3 Reduced Gas Analyzer
- Dohrmann Low-Level TOC Analyzer
- HACH COD and N digesters

- Packard 1900TR Scintillation Counter
- Hitachi V2000 UV/vis Spectrophotometer

MONTGOMERY WATSON

Montgomery Watson is an environmental engineering firm with corporate headquarters located in Pasadena, California. Although it does business in all aspects of environmental engineering, the firm is most known for its strength in water treatment. Specifically, Montgomery Watson's Applied Research Department has been conducting water treatment bench- and pilot-scale studies for water utilities across the United States for the past 12 years.

As noted earlier, Montgomery Watson will provide engineering support in the form of engineering and economic feasibility analysis of the proposed biological process based on the information obtained during the bench-scale testing at Northwestern University. Montgomery Watson will also develop the proposed pilot testing program for Phase II of the project, which will focus on obtaining field data on the performance, operation, and maintenance requirements of the biological process. Montgomery Watson's Applied Research Department is highly qualified for conducting these activities. The Department owns a 7,000-ft^2 facility in Southern California that is dedicated to the design, construction, and maintenance of the company's pilot-scale testing equipment. The Department staff are specialized in conducting treatability studies for both water and wastewater treatment. Specifically, as noted earlier, Montgomery Watson's Applied Research Department is currently conducting a treatability study on the removal of perchlorate from groundwater using ion-exchange. The project includes pilot scale testing of the process, as well as the application of biological treatment for the removal of the concentrated perchlorate from the spent regeneration brine solution.

SECTION 7
BUDGET

BUDGET FOR BIOLOGICAL PERCHLORATE REMOVAL PROJECT

ITEM	AWWARF	*In Kind*†††	TOTAL
Personnel			
B.E. Rittmann	$ 13,300.	$ 9,600.[1]	$ 22,900.
Grad. R.A. (1)	40,500.	0.	40,500.
Hourly Help	2,000.	0.	2,000.
Lab Coordinator	3,000.	0.	3,000.
Total Personnel	$ 58,800.	$ 9,600.	$ 68,400.
Benefits (19.25%)	$ 11,319.	$ 1,848.	$ 13,167.
Total Sal., Wages, Benefits	$ 70,119.	$ 11,448.	$ 81,567.
Equipment†	$ 0.	$ 5,000.[1]	$ 5,000.
Expendable Materials and Supplies	22,000.	6,000.[1]	28,000.
Maintenance	4,000.	0.	4,000.
Reproduction/Drafting/Mailing	1,500.	0.	1,500.
Telecommunications	300.	0.	300.
Travel	4,500.	0.	4,500.
Services/Fabrication	1,000.	2,000.[1]	3,000.
Analytical Services	0.	17,000.[2]	17,000.
Tuition†	0.	28,700.[1]	28,700.
Subcontract (Montgomery-Watson)††	109,900.	3,000.[3]	112,900.
Total Exp. and Equip.	$ 143,200.	$ 61,700.	$ 204,900.
Total Direct Costs (TDC)	$ 213,319.	$ 73,148.	$ 286,467.
Indirect Costs			
48% of (Modified TDC + $25,000 of subcontract)			
Total Indirect Costs	$ 61,641.	$ 18,935.	$ 80,576.
GRAND TOTAL	$ 274,960.	$ 92,083.	$ 367,043.

† Not included in the Modified TDC.

†† Only the first $25,000 is included in the Modified TDC.

††† *In Kind* is from Northwestern University[1], the utilities[2], or Montgomery-Watson[3].

APPENDICES

APPENDIX A
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APPENDIX B
DENITRIFICATION REPORT

A Review of Biological Denitrification of Drinking Water

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Chapter 1. Introduction

Removing nitrates (NO_3^-) and nitrites (NO_2^-) is becoming increasingly important because of the risk posed to human health from nitrate contamination of groundwater and surface water. Excessive nitrate and nitrite in drinking water is known to cause methemoglobinemia (the "blue-baby syndrome") in infants (Bouchard et al., 1992). Nitrite, which is the reduced product from nitrate by human microflora, is the actual agent that combines with hemoglobin and precludes the transport of oxygen by blood. Under favorable conditions, nitrate also can react with secondary amines to form N-nitroso compounds, which are highly carcinogenic (Hiscock et al., 1991; Bouchard et al., 1992). Therefore, USEPA has set the maximum contaminant levels (MCL) of 10 mg NO_3^--N/l and 1 mg NO_2^--N/l. The European standard for nitrite is much more strict (0.03 mg NO_2^--N/l) to account for the toxic effect from nitrite (Urbain et al., 1996).

Excessive nitrate is frequently found in drinking water supplies. A 1985 AWWA survey showed that 23 percent of the violations of primary drinking water standards were the result of excessive nitrate (Montgomery, 1985). These contaminations are generally caused by agricultural use of fertilizers, and the leaching of nitrate into groundwater and surface water is enhanced by crop irrigation. The frequency of nitrate MCL violations, as well as levels of contamination, appears to be increasing (ICRC, 1993). Estimates based on data collected in the USEPA National Pesticides Survey indicate that 5 percent of public and private wells have nitrate concentrations greater than the USEPA MCL of 10 mg NO_3^--N/l (Bouchard et al., 1992). Thus, nitrate contamination is an important and growing water-quality problem that must be remedied.

Physical-chemical and biological treatment processes are used to remove nitrate and nitrite in the drinking-water supplies. Previous experiences with physical-chemical treatment methods include ion exchange, reverse-osmosis, activated-carbon adsorption, and electrodialysis (ICRC, 1993; Dahab, 1987). Ion exchange, which is the most economic and widely used one among these methods, frequently suffers from several

problems, such as: the regeneration process of ion-change resins uses a large amount of salt, organics foul the resins, the waste solution from regeneration must be disposed of, and competition from other anions, such as SO_4^{2-} and HCO_3^-, reduces the efficiency of NO_3^- removal (Philipot and de Larminat, 1988; Godart and Gonnard, 1991).

The biological process that removes nitrate and nitrite is denitrification, which reduces nitrate and nitrite to nitrogen gas (N_2). Denitrification has been used to remove nitrate directly or to remove concentrated nitrate in waste brine effluent from ion-exchange processes. Because it has none of the drawbacks of ion exchange and is substantially less expensive, direct denitrification is a promising treatment process. The Inorganic Contaminants Research Committee of the AWWA Research Division (ICRC, 1993) pointed out key research needs regarding the drinking-water denitrification process: use of inorganic electron donors in denitrification, kinetics of nitrate loss and nitrite formation or consumption, and factors influencing nitrate removal in different biofilm systems, such as different media. This study targets on these guidelines and critically reviews the current alternatives for biological denitrification and past experiences for these denitrification processes. Also, a design procedure for a biofilm reactor using the normalized-loading-curve (NLC) technique, illustrated through a design example for a denitrifying biofilm reactor using an organic or an inorganic electron-donor substrate, shows the influence of the different substrates on the design results.

Chapter 2. Background

2.1 An overview of nitrate reduction

Nitrate present in the environment can be reduced biologically following several pathways: respiratory dissimilatory denitrification, dissimilatory nitrate reduction to ammonium, and assimilatory nitrate reduction (Tiedje, 1988). The pathways for the three mechanisms are shown in Table 1. Dissimilatory nitrate reduction is distinct from assimilatory nitrate reduction by the fact that the reduced nitrogen species are not utilized for the cell synthesis, i.e., nitrate or nitrite is not directly utilized as the nitrogen source for growth in the dissimilatory pathway. Instead, the energy gained from reduction of nitrogen oxide in dissimilatory processes is utilized for growth and maintenance of the organisms.

Table 1. Processes of biological nitrate reduction (from Tiedje, 1988).

Mechanism	Pathway	Regulator	Process carried out by:
Assimilatory nitrate reduction	$NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+$	NH_4^+, organic N	Plants, fungi, algae, bacteria
Dissimilatory nitrate reduction to ammonium	$NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+$	O_2	Anaerobic, facultative anaerobic bacteria, and some aerobic bacteria
Denitrification (dissimilatory)	$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$	O_2	Aerobic and facultative anaerobic bacteria grow with NO_3^- or NO_2^-

Assimilatory nitrate reduction is the reaction in which nitrate is reduced to ammonium (NH_4^+) with nitrite being the intermediate. As an assimilative metabolism, only enough nitrate is reduced to satisfy the needs for nutrient to support growth. The NH_4^+ is synthesized into organic nitrogen and eventually becomes part of the cell structure. This reaction, which is regulated by NH_4^+ and organic nitrogen, is carried out by many plants, fungi, algae, and bacteria. This mechanism is of limited engineering significance because, in many cases, net synthesis of new biomass is small, which means that most ammonium

and organic nitrogen can be supplied through the breakdown of biomass. Thus, net removal of N due to assimilation often is low and cannot be used for a nitrate-removal technology.

Dissimilatory nitrate reduction to ammonium, which has the same free intermediates (NO_2^-) and product (NH_4^+) as in assimilatory nitrate reduction, is carried out by different enzymes and is regulated differently, i.e., by O_2 (Payne, 1973). The eight electrons yielded per nitrogen reduced (NO_3^-:N oxidation state=+5 to NH_4^+:N oxidation state=-3) from this reaction make it very favorable in anaerobic environments where the electron-acceptor substrate (nitrate) is limited (King and Nedwell, 1985). This indicates that an environment with high e^--donor to e^--acceptor substrate ratio should be strongly selective for dissimilatory nitrate reduction to ammonium. Organisms that are capable of dissimilating nitrate to ammonium includes some obligate anaerobes (such as *Clostridia* and some rumen bacteria), facultative anaerobes (like the Enterobacteriaceae members), microaerophilic bacteria, and a few aerobic bacteria, such as several strains in *Pseudomonas* and *Bacillus* (Tiedje, 1988). The low concentration of electron donors in the drinking water application suggest that dissimilatory nitrate reduction to ammonium will not be important.

Denitrification is a respiratory process in which the reduction of nitrate and nitrite to N_2 is coupled to electron-transport phosphorylation. It is a major mechanism in the global nitrogen balance by transforming fixed nitrogen to nitrogen gas and completing the nitrogen cycle. The denitrification process is regulated by O_2. However, all the denitrifiers are facultatively aerobes, i.e., they are able to grow on oxygen and, alternatively, nitrate and nitrite when oxygen becomes limiting. In fact, a gradual shift from aerobic respiration to nitrate respiration is beneficial to the growth of denitrifiers, because it allows the bacteria to generate energy for the synthesis of required denitrifying enzymes (Aida et al., 1986; Körner and Zumft, 1989). This ability to carry out aerobic

and denitrifying respirations offers a great advantage for engineering applications, since a careful maintenance of strictly anaerobic environment is not required. Denitrifying microorganisms are known to use organic (organotrophs), inorganic (lithotrophs), or light (phototrophs) as their energy source. Denitrifiers are commonly found in soils, groundwater, sediments, and wastewater treatment plants. Some denitrifiers are even isolated from boiled ox blood and oil brine (Zumft, 1992). The metabolism, distribution, and application of denitrifiers will be discussed in the following section. Classical denitrification using organic or inorganic electron donors has great promise for drinking-water treatment and already is being used on a limited basis.

Abiotic nitrogen-gas-generating reactions (chemodenitrification), which are catalyzed by abiologic agents, can also occur in the environment. The most significant reaction among this category is the reduction of nitrite to nitric oxide (NO), nitrous oxide (N_2O), and N_2 under acidic environment (pH<5), with NO being the most abundant product (Van Cleemput et al., 1976). Since these reactions usually occur in extreme conditions, such as nitrite-containing acid or frozen soils, they are not of importance for drinking-water treatment.

2.2 Denitrification

In denitrification, nitrate or nitrate is reduced sequentially to nitric oxide, nitrous oxide, and nitrogen gas. A summary of the sequential reactions, number of electron transferred, change of N oxidation state, and the free energy change is given in Table 2. Each stepwise reduction of nitrogenous oxides is catalyzed by a specific enzyme, namely nitrate reductase (NaR), nitrite reductase (NiR), nitric-oxide reductase (NOR), and nitrous-oxide reductase (N_2OR) (Ye et al., 1994).

Denitrification is widely spread throughout different taxa of bacteria, such as *Archaebacteria* (within the genera *Halobacterium*, *Haloferax*, and *Haloarcula*), *Proteobacteria* (subclass alpha, beta, and gamma), and some species in gram-positive

Table 2. Sequential reactions of denitrification (after Zumft, 1992).

Reaction/Enzyme	Number of e^- exchanged	Oxidation state change of N	Free energy change, $\Delta G_o'$ (kJ/mol N)[a]
(1) Nitrate reduction / NaR $NO_3^- + H_2 \rightarrow NO_2^- + H_2O$	2	$+5 \rightarrow +3$	-161.1
(2) Nitrite reduction / NiR $NO_2^- + 0.5H_2 + H^+ \rightarrow NO_{(g)} + H_2O$	1	$+3 \rightarrow +2$	-76.2
(3) Nitric oxide reduction / NOR $2NO_{(g)} + H_2 \rightarrow N_2O_{(g)} + H_2O$	2 (1/N)	$+2 \rightarrow +1$	-306.3
(4) Nitrous oxide reduction / N_2OR $N_2O_{(g)} + H_2 \rightarrow N_{2(g)} + H_2O$	2 (1/N)	$+1 \rightarrow 0$	-339.5
(5) Overall reaction from NO_3^- to N_2 $2NO_3^- + 2H^+ + 5H_2 \rightarrow N_2 + 6H_2O$	10 (5/N)	$+5 \rightarrow 0$	-1121.2

[a] Referenced to the oxidation pair $H_2/2H^+$ with pH=7.

Eubacteria (*Bacillus* species) (Zumft, 1992). Physiologically, denitrifiers can use organic carbon as their energy and carbon source (heterotrophs), inorganic compounds (hydrogen, sulfur, and ammonium) as the energy source and CO_2 as the carbon source (autotrophs), and light as the energy source (phototrophs). Among the denitrifiers, heterotrophic bacteria are the most abundant group and encompass the *Pseudomonas* sp., *Alcaligenes* sp., *Paracoccus* sp., *Aquaspirillum* sp., *Bacillus* sp., *Halobacterium* sp., *Rhizobium* sp., and *Neisseria* sp. (Tiedje, 1988; Zumft, 1992). Only a very limited group of denitrifying organisms is autotrophic: These include the H_2 oxidizers (*Paracoccus denitrificans*, *Alcaligenes eutrophus*, *Pseudomonas pseudoflava*, and *Bradyrhizobium*) (Bowien and Schlegel, 1981; Aragno and Schlegel, 1992; Auling et al., 1978; Willems et al., 1989; Klüber et al., 1995), S oxidizers (*Thiobacillus denitrificans*, *Thiobacillus versutus*, and *Thiosphaera pantotropha*), and NH_4^+ *oxidizers (Nitrosomonas europeae* which form N_2O from NO_2^-; one strain also forms N_2), and phototrophic bacteria (*Rhodobacter sphaeroides*, *Rhodopseudomonas palustris*, and *Erythrobacter* sp. Och114) (Harrison, 1983; Michalski et al., 1986; Tiedje, 1988).

Although most of the bacteria are capable of reducing NO_3^- to N_2, incomplete denitrification has been found in many bacterial species. Some bacteria are strict nitrite respirers (lack nitrate reductase), some cannot reduce N_2O to N_2, and one species, *Wolinella succinogenes*, lacks the ability to reduce NO_2^- to N_2O (Yoshinari, 1980). In natural environment and engineering systems where a mixed group of organisms possesses various capabilities for performing intermediate steps within the denitrification reaction train, these partial denitrifiers may play a role for keeping the overall reaction well-balanced. Indeed, being a highly organized process involving a genetically diverse and metabolically-versatile group of microorganisms, denitrification can be influenced by many physicochemical factors that affect the microbial ecology.

2.3 Factors controlling the performance of denitrification

In general, the performance of a denitrification process is controlled by several physicochemical factors, such as the loadings of particular substrates and intermediates, the O_2 concentration, the pH, the temperature, and the electron donor substrate. Improper control over these factors can lead to accumulation of intermediates, i.e., NO_2^-, NO, and N_2O, which frequently exert toxic effects on microbial growth and denitrifying enzymes. For instance, NO_2^- and NO have high affinity to metal ions (like iron, copper, and molybdenum), which are importance constituents for denitrifying enzymes. NO is known to be inhibitory to NiR and NO_2R (Dhesi and Timkovich, 1984; Frunzke and Zumft, 1986). A high nitrite concentration can also promote formation of NO and, therefore, adversely affect the microbial activities (Anderson and Levine, 1986; Zafiriou et al., 1989; Goretski et al., 1990; Goretski and Hollocher, 1988). In fact, nitrite accumulation is the most widely occurring problem in water denitrification systems.

2.3.1 Substrate and intermediate loadings

A complete denitrification process is highly dependent on a well-balanced rate for different participating reactions (Betlach and Tiedje, 1981; Thomas et al., 1994). Nitrate at a high concentration, as well as a shock addition of nitrate to the denitrifying system, can lead to an elevation of nitrite concentration. Betlach and Tiedje (1981) used a pure culture of *Pseudomonas fluorescens* and found that the rate of nitrate reduction (19.1 μM/min) was approximately two-fold greater than the rate of nitrite reduction (10.7 μM/min) in a batch study with an initial NO_3^- concentration of 0.5 mM. This misbalance can lead to accumulated NO_2^- in a highly loaded system, which can cause growth uncoupling of microorganisms from the denitrification activity and can decrease the overall reaction rate (Almeida et al., 1995a). Alternatively, a high nitrite concentration can create a high nitrite reductase reaction rate, causing a higher production rate and

accumulation of N_2O (Thomas et al., 1994; Schulthess and Gujer, 1996), which is a potential greenhouse gas and is involved in the chemical destruction of the ozone layer, both of which influence the global climate (Badr and Probert, 1993).

The electron donor substrate plays two key roles in a denitrifying reactor system. First, the electron donor is utilized by denitrifiers to consume oxygen and create an anoxic environment for denitrification to occur. Second, the electron donor provides energy to drive the sequential denitrification reactions. Therefore, as the stepwise denitrification reactions proceed, it is important to maintain the electron-donor concentration at a certain level for complete denitrification. Too little electron donor relative to nitrate and other N oxides concentrations can result in a decrease in reaction rate or a cessation of the stepwise reactions at NO_2^- or N_2O (mostly NO_2^-), which causes accumulation of intermediates (Tiedje, 1988; Hamon and Fustec, 1991; Bernet et al., 1995; Wilderer et al., 1987).

In drinking water, electron donor substrates are always too low to drive denitrification, and it is necessary to add a supplementary electron donor. On the other hand, overdosing electron donor to the denitrifying system can create many problems (explanation will be given in section 2.3.5). Therefore, maintaining an optimum electron-donor concentration without accumulating nitrite becomes a critical challenge in drinking water denitrification.

A second critical challenge is maintaining relatively steady-state substrate loadings and allowing enough retention time to clear intermediates in denitrifying reactor systems. A reactor that needs occasional backwashing, such as a packed-bed column reactor, may not be suitable for denitrification, since nitrite accumulation can occur immediately after backwash, when fresh nitrate is suddenly reintroduced into a reactor that has lost a significant portion of its biomass. In all cases, sufficient retention time is necessary to allow complete nitrite reduction and subsequent steps.

2.3.2 O_2 concentration

It is generally assumed that oxygen is the major regulator for denitrification activity and has been studied by many researchers using pure cultures (Kröger and Winkler, 1981; Körner and Zumft, 1989; Thomas et al, 1994) and treatment systems (Rittmann and Langeland, 1985; Simpkin and Boyle, 1988; Lie and Welander, 1994; Shulthess et al., 1994). The range of oxygen levels for detectable denitrification to occur spans from 90% air saturation for *Thiosphaera pantotropha* to 53% air saturation for *Alcaligenes* sp. to almost anaerobic conditions for *Paracoccus denitrificans* (Robertson and Kuenen, 1984; Krul and Veeningen, 1977; Alefounder et al., 1981). However, low denitrification rates and accumulation of intermediates usually occur in these marginal conditions.

Oxygen is known to control denitrification at two levels: repression of enzyme synthesis and inhibition of enzyme activity. Generally, synthesis of denitrifying enzymes is permitted at higher oxygen concentrations than the threshold for activity of these enzymes. This situation allows the bacteria to be prepared for immediate use of nitrate when the O_2 concentration declines. Körner and Zumft (1989) showed that the critical regions for NaR, NiR, and N_2OR expression were <5.1, <2.5, and <3.8 mg O_2/l, respectively, for *Pseudomonas stutzeri* growing on nitrate. (Recall Table 2 for definitions of the reactions catalyzed by each enzyme.) An O_2 concentration at 0.6 mg/l gave the maximum enzyme expression. This indicates that, at the onset of denitrification and when the dissolved O_2 concentration in a system is still high, nitrite has the greatest tendency to accumulate, since its expression requires the lowest O_2 concentration.

Tiedje (1988) reported that the approximate inhibitory ranges of O_2 concentration for NaR, NiR, and N_2OR activity are 0.28-0.42, 0.12-0.28, and 0.02-0.14 mg O_2/l. The threshold O_2 concentration for whole cells was found to be around 0.2-0.3 mg/l (Rittmann and Langeland, 1985; Tiedje, 1988). In water treatment systems, however, the O_2

concentration that limits denitrification can be much higher, because the denitrifiers are almost always located within a bacterial aggregate (Rittmann and Langeland, 1985). For instance, in biofilm processes, gradual consumption of oxygen in the outer biofilm allows the inner part of biofilm to be anoxic and denitrifying activity to be active. The distance from the bulk water-biofilm surface to the denitrification zone is dependent on the bulk O_2 concentration and the rate of e^--donor-substrate supply.

2.3.3 pH

The optimum pH for denitrification appears to be 7 to 8 (Knowles, 1982; Thomas et al., 1994; Almeida et al., 1995b), although denitrification can occur up to a pH of 11 (Prakasam and Loehr, 1972). pH outside of the optimum range may cause accumulation of intermediates. Generally, nitrite is accumulated at alkaline pH, while nitrous oxide is accumulated at acidic pH (Thomas et al., 1994; Thomsen et al., 1994; Bernet et al., 1995).

Since denitrification consumes H^+ (1 mole H^+ per mole of NO_3^- reduced to N_2), the pH of the system may rise as denitrification proceeds. The degree to which the pH rises depends on the buffering intensity, which generally is supplied by bicarbonate alkalinity. When alkalinity is not very high and especially when denitrification reactions are very intensive, the pH rise can be substantial. For instance, the pH inside a denitrifying biofilm was predicted to be 9.5-12, although the pH in the bulk solution was 7 (Arvin and Kristensen, 1982; Sakakibara et al., 1994b). Due to the difficulty measuring pH inside the biofilm, these pHs were model-predicted values. Nevertheless, these data suggest that the denitrification activity can be partially controlled by pH in biofilms, especially the region close to the biofilm-particle interface, where diffusion resistance slows the replenishment of buffering ions within the biofilm.

2.3.4 Temperature

The rate of denitrification increases as temperature increases, reaches a maximum rate at temperature around 60 to 75 °C, and then declines rapidly (Knowles, 1982). The reaction rates at different temperatures generally follows the linearized form of the Arrhenius equation below the optimum temperature:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right) \tag{2-1}$$

where k_1 and k_2 are the reaction rate at temperature T_1 and T_2 (°K), E_a is the Arrhenius constant (cal/mol), and R is the universal gas constant (1.9872 cal/mol-K). The value of E_a for denitrification is approximately between 10 to 19.5 kJ/mole (summarized by Lewandowski (1982) based on the results of several studies in activated sludge, packed column, and batch tests at temperature between 3 and 25 °C). For the experiment carried out by Lewandowski (1982), who studied denitrification in activated sludge with methanol, acetone, and acetate as the e^--donor substrates at temperature between 2.5 and 35 °C, E_a was between 10.9 and 11.8 kJ/mol.

2.3.5 Choice of electron donor substrate

As mentioned before, the amount of e^--donor substrate present in drinking-water supplies is never enough to drive the complete denitrification reaction. Therefore, addition of an organic (heterotrophic denitrification) or inorganic (autotrophic denitrification) electron donor is necessary for the microorganisms to grow. For heterotrophic denitrification, ethanol (Chang et al., 1993; Green et al., 1995; Urbain et al., 1996), methanol (Liessens et al., 1993; McCleaf and Schroeder, 1995), and acetate (Lazarova et al., 1992) are the most common and well-studied e^--donor substrates for drinking water. For autotrophic denitrification, H_2 is an excellent choice because of its clean nature, low biomass yield, and relatively low cost (Dries et al., 1988; Gros et al.,

1988; Kurt et al., 1987; Tuisel et al, 1989). A reduced sulfur compound, mainly pelletized element sulfur (i.e., S^o), is the other viable autotrophic electron donor.

Addition of organic e^--donor substrate to the water supplies for denitrification has several disadvantages, which originate from the after-process residuals due to overdosing or variation of influent nitrate concentration. First, acute toxic effects to human can occur if methanol is not totally removed in the effluent (Keyvan-Larijarni and Tannenberg, 1974). Second, residual organic compounds in water-distribution systems promote excessive microbial growth in the pipelines, which in turn causes increasing plate counts and taste and odor of the finished water, and corrosion and decreasing hydraulic capacity of the pipelines (Rittmann and Huck, 1989). Normally, the inorganic electron donors do not persist in the effluent. H_2 evolves to the air, while S is very slightly soluble.

Third, the true yield (Y), expressed as g cells/g oxygen demand (OD) of e^- donor, from heterotrophic denitrification is much higher than that for autotrophic denitrification. Table 3 summarizes the stoichiometry of heterotrophic denitrification using ethanol, acetate, and methanol, and autotrophic denitrification using H_2 and S. This stoichiometric relationship between e^- donor/e^- acceptor and biomass (expressed as $C_5H_7O_2N$) is based on the concepts derived by McCarty (1972). The Y value for autotrophic denitrification using H_2 (i.e., autohydrogenotrophic denitrification) is 0.107 g cells/g OD of e^- donor, which is 44% to 75% of the Y for heterotrophic denitrification using the common organic substrates. This lower yield offers a great advantage for drinking water treatment, because the biomass ultimately must be wasted from the system via backwashing or in the process effluent.

Table 3. Stoichiometry and true yield for heterotrophic denitrification using ethanol, methanol, and acetate and autotrophic denitrification using H_2 and S.

Reaction No.	e^-- donor substrate	Stoichiometric reaction	Y (g cells/g OD e^- donor)
1	Ethanol (C_2H_5OH)	$0.69C_2H_5OH + NO_3^- + H^+ \rightarrow 0.14C_5H_7O_2N + 0.43N_2 + 0.67CO_2 + 2.07H_2O$	0.241
2	Methanol (CH_3OH)	$1.08CH_3OH + NO_3^- + H^+ \rightarrow 0.065C_5H_7O_2N + 0.47N_2 + 0.76CO_2 + 2.44H_2O$	0.142
3	Acetate (CH_3COO^-)	$0.986CH_3COO^- + NO_3^- + H^+ \rightarrow 0.125C_5H_7O_2N + 0.44N_2 + 0.36CO_2 + 1.047H_2O + 0.99HCO_3^-$	0.225
4	Hydrogen (H_2)	$3H_2 + NO_3^- + H^+ + 0.228CO_2 \rightarrow 0.0456C_5H_7O_2N + 0.47N_2 + 3.34H_2O$	0.107
5	Sulfur (S^o)	$0.98S + NO_3^- + 0.609H_2O + 0.188CO_2 \rightarrow 0.0375C_5H_7O_2N + 0.48N_2 + 0.98SO_4^{-2} + 0.955H^+$	0.068

Chapter 3. Past Experiences for Denitrification of Drinking Water

As is true for most of biological drinking-water treatment (Rittmann and Huck, 1989; Rittmann, 1995; Bouwer and Crowe, 1988), almost all denitrification processes employ a biofilm system as the strategy for biomass retention. Biofilm processes offer many powerful advantages for drinking-water treatment over a suspended-growth system. The most important advantage is the naturally occurring good cell retention by having high-density cell accumulation onto a large surface. This is a particularly beneficial situation when the substrate concentration is low and the cell accumulation is difficult. The former is especially true for drinking water applications, and the latter is generally true for autotrophic bacteria. Good cell retention also increases the removal capacity per unit volume of reactor and makes the process economical. Finally, excellent cell retention minimizes the amount of biomass that leaves the biofilm system with the treated water.

3.1 Previous experiences with heterotrophic denitrification

Heterotrophic denitrification has been the most common strategy for drinking water denitrification, primarily because of its wide and successful use in wastewater denitrification. Experiences from some full-scale and pilot-scale studies are summarized in Table 4.

The "Biodenit," "Nitrazur," and "Biocristal-DN" denitrification processes were developed in France (Richard, 1989; Mateju et al., 1992; Urbain et al., 1996). The first full-scale drinking water denitrification plant was built in Eragny and commissioned in June, 1983 (Philipot et al., 1985). The treatment plant employed the Biodenit process, which was based on a downflow anaerobic bioreactor packed with an expanded clay (Biodagène) onto which heterotrophic bacteria were attached. Ethanol was used as the carbon and energy source, and phosphorus was the nutrient and buffer. This 80 m^3/hr system was designed to treat 1.2 kg NO_3^--N/m^3-d and reduce the NO_3^--N concentration from 15 to 6 mg/l. The follow-up treatment of the denitrified water included an aerated

Table 4. Previous studies in heterotrophic denitrification of drinking water.

Parameter	Eragny, France (Biodenit)	Dennemont, France (Biodenit)	Chateau Landon, France (Nitrazur)	Champfleur, France (Nitrazur)	Douchy, France (Biocristal-DN)
Flow rate, m^3/hr	80	400	50	35	17
Media type	Biodagène[a]	Biodagène[a]	Biolite L[b]	Biolite L[b]	Suspended-growth system
Diameter, mm	3-6	3-6	1.7	2.7	
Inoculum microorganism	Heterotrophic mixed culture	Heterotrophic mixed culture	not described	not described	not described
Bed type	Fixed, downflow	Fixed, downflow	Fixed, upflow	Fixed, upflow	-
Surface area, m^2	9.8	32	6.4	8.5	-
Carbon source	Ethanol	Ethanol	Acetate/Ethanol[c]	Ethanol	Ethanol
Influent NO_3^--N concentration, mg N/l	15	15	18	16	12
Effluent concentrations					
NO_3^--N, mg N/l	6	4	6	5	2.3
NO_2^--N, mg N/l	<0.02	0	<0.03	0	<0.02
C, mg/l	not available	not available	not available	not available	0.8 as DOC
g C-source/g N	not available	1.2	4-7 (w/ acetate)	3.1	3.3
NO_3^--N elimination rate, $gm^{-3}d^{-1}$	1,200	not determinable[f]	not determinable	not determinable	100
C-source loading rate, $gCODm^{-3}d^{-1}$	3,000[d]	not determinable	not determinable	not determinable	690
C-source surface loading, $gCODm^{-2}d^{-1}$	4,400[d]	8,300	13,400	7,000	not relevant
J/J_R[e]	6,800	12,700	20,700	10,800	not relevant

[a] Expanded clay.
[b] Expanded clay.
[c] Carbon source was switched to ethanol when the price of acetate was not competitive.
[d] Based on the g C-source/g N value (1.2) from the Dennemont, France case.
[e] Base on J_R= 0.65 $gCODm^{-2}d^{-1}$ (see section 4.3).
[f] Not determinable based on the information provided in the literature.

Table 4. Continued.

Parameter	Monheim, Germany (Denipor)	De Blankaart, Belgium	Green et al., 1994
Flow rate, m^3/hr	300	40	0.02
Media type Diameter, mm	Styropor spheres not available	Sand 0.25-0.5	Sludge granule 3
Inoculum microorganism	Indigenous bacteria in groundwater	Indigenous bacteria in surface water	Indigenous bacteria from WWTP and lab USB reactor
Bed type	Fixed	Fluidized	Sludge blanket
Surface area, m^2	not available	2	-
Carbon source	Ethanol	Methanol	Ethanol
Influent NO_3^--N concentration, mg N/l	not available	17	23
Effluent concentrations NO_3^--N, mg N/l NO_2^--N, mg N/l C, mg/l	 <2.3 not available not available	 0 0 1-2 as methanol	 2.3 0 0 (as ethanol)
g C-source/g N	not available	2.9	2.2
NO_3^--N elimination rate, $gm^{-3}d^{-1}$	1,000	2,030	4,000
C-source loading rate, $gCODm^{-3}d^{-1}$	4,740[g]	8,800	18,300
C-source surface loading, $gCODm^{-2}d^{-1}$	not determinable	35,000	not relevant
J/J_R	not determinable	53,700	not relevant

[g] Based on the g C-source/g N value (2.27) derived from Table 3.

two-layer activated carbon and Biocarbone filter with coagulant addition to remove excess carbon and micropollutants, ozonation, and chlorination. The final concentration of nitrite was kept below 0.02 mg N/l.

After testing the facility in Eragny, another 400 m^3/hr Biodenit installation was built at Dennemont and started in 1987. The nitrate removal efficiency was 74% (15 to 4 mg N/l) with an ethanol dose of 1.2 g/g NO_3^--N removed. Nitrite was not detected in the effluent. The sludge production was 32 kg/d and was discharged to a sewage works.

Another French process is Nitrazur, and the first unit was constructed in 1983 at Chateau Landon (Frick and Richard, 1985). The 50 m^3/hr facility consisted of an upflow fixed-bed reactor packed with an expanded clay (Biolite L), flocculant addition, carbon filtration, and chlorination. Acetate was used as the carbon source. As the price of ethanol became more advantageous, the electron donor was switched to it. Nitrate concentrations were reduced from 18 to 6 mg N/l. Nitrite accumulated immediately after start-up, but decreased to less than 0.03 mg N/l after process equilibrium was reached.

Based on the Chateau Landon experiences, another Nitrazur plant was built at Champfleur, France. This 35 m^3/hr facility yielded a nitrate removal efficiency of 72% with an ethanol dose of 3.1 g/g NO_3^--N removed (Hiscock et al., 1991). Operational experience showed that the reactor and activated carbon filter had to be thoroughly washed between production cycles to avoid generation of nitrite. A typical cycle lasted 48 hrs with 1 hr for washing.

Recently, another French process, named Biocristal-DN, was built at Douchy and started in March 1995 (Urbain et al., 1996). The Biocristal-DN process is a combination of membrane bioreactor technology (MBR) and powdered activated carbon adsorption. The MBR denitrification process is essentially a completely-mixed, suspended-growth bioreactor followed by an ultrafiltration device using double-skin hollow fiber membranes made of a cellulosic derivative. Denitrification used ethanol as the electron donor and carbon source, natural organic matter and pesticides were removed by activated carbon

adsorption, and disinfection was by ultrafiltration. Finally, chlorine was added to the ultrafiltered water to maintain quality in the distribution system. This 17 m^3/hr facility reduced the nitrate concentrations from 12 to 2.3 mg N/l with a loading rate of 0.1 kg NO_3^--N/m^3-d. This loading rate, low compared with the full-scale fixed biofilm processes, such as the Eragny and Dennemont installations, was due to the high tangential crossflow velocity for the ultrafiltration unit needed to separate the high concentration of suspended biomass, which was caused by the high nitrate loading and the high yield from ethanol. The ethanol dose added to the raw water was 3.3 g/g NO_3^--N removed. The nitrite concentration in the treated water was lower than 0.02 mg N/l.

A fixed-film biological denitrification process using ethanol as the carbon source and buoyant Styropor spheres as bacteria carriers was developed in Germany and given the trade name "Denipor" (Roennefahrt, 1985; Roennefahrt, 1986). This 300 m^3/hr facility, built at Monheim, Germany, employed 4 Denipor bioreactors in series. The post treatment included two steps. The first step was aeration with four aerobic fixed-bed filters with gaseous oxygen addition. The second step was an aerobic filtration in two fixed-bed filters packed with activated carbon. The treated water was disinfected with addition of chlorine dioxide. The facility was capable of removing 80 kg NO_3^--N/d and the NO_3^--N in the effluent was below 2.3 mg/l. A 95% nitrate removal efficiency was achieved by a loading rate of 1 kg NO_3^--N/m^3-d and a recirculation rate of 200-500%.

The denitrification facility at the De Blankaart drinking water production center in Belgium is a pilot-scale fluidized-bed reactor using methanol as the electron-donor substrate and sand particles as the biofilm carrier (Liessens et al., 1993). This plant had a capacity of 40 m^3/hr and achieved complete nitrate removal for surface water with 17 mg N/l. This corresponded to a nitrate loading rate of 2 kg NO_3^--N/m^3-d with a methanol dose of 2.9 g per g of nitrate nitrogen removed. Nitrite was not detected in the effluent provided there was a 1 to 2 mg/l of residual methanol. This excess methanol was removed by the downstream water treatment process. A significant effort was put into the on-line

methanol monitor for the control of methanol dosage; due to the toxicity of methanol, it was necessary to minimize the breakthrough of methanol into the reactor effluent and the various stages of postdenitrification process.

Green et al. (1994) reported the results of denitrification of groundwater using a 2.8-liter lab-scale upflow sludge blanket (USB) reactor. The USB reactor used water upflow through a layer of sludge aggregates, and no carrier was used. The formation of high-density granulated sludge, which depends on the type of substrate used, is essential for achieving an efficient process. This lab-scale 0.02 m^3/hr USB reactor was capable of reducing the nitrate concentration from 23 to less than 2.3 mg N/l. The maximum nitrate loading rate was 4 kg NO_3^--N/m^3-d with a retention time of 8 min. The ethanol-to-nitrogen weight ratio had to be above 0.5 in order to avoid nitrite accumulation for continuous operation.

During the experiments, a "harder" water (with hardness of 380-450 mg/l as $CaCO_3$) and a "softer" water (with hardness of 150-380 mg/l as $CaCO_3$) were tested. The results showed that the "harder" water formed round-shaped granules (3 mm diameter) and caused a high biomass density (30-40 gVSS/l) and good sludge settlability. However, for the "softer" water, the granules were of oblong shape, larger in size, and less dense than that for the "harder" water, and they exhibited poor filterability and a tendency to float. The biomass washout from the reactor was a serious problem for the "softer" water experiment due to the floating sludge. Therefore, the USB denitrification has some severe limitations on the raw water composition and could be restricted to high-hardness waters.

The high loadings of the electron donor substrate, together with the high surface loadings (J) and the high normalized loadings J/J_R (section 4.2 describes J, J_R, and J/J_R), imply that the systems shown in Table 4 were operated in high-loading regions, which are associated with high electron-donor substrate concentrations in the effluent (discussed in section 4.2). Therefore, post-treatment was required to remove excessive electron-donor substrate and provide a biologically stable water (Rittmann and Huck, 1989).

In summary, heterotrophic denitrification can effectively remove nitrate from the water, but post-treatment of denitrified water to remove the residual carbon appears to be necessary to prevent bacterial after-growth during distribution. The Biocristal-DN process minimized this situation by partially removing the nitrate and keeping the ethanol concentration low (as the limiting substrate), but the nitrate loading was low because of the restriction on flow velocity of ultrafiltration unit by high biomass concentration when the nitrate loading is high.

The U.S. experience with biological denitrification has not yet been significant. One reason for slow acceptance may be the fear of bacterial contamination in the treated water. Some researches (not included in Table 4) have focused on solving this problem using immobilized microorganisms within gel or special materials to prevent biomass loss to the treated water (Nilson and Ohlson, 1982; Kokufuta et al., 1986; Lemoine et al., 1988). However, when the system is operated continuously, it is impossible to avoid formation of a biofilm on the outside of the particles of immobilized microorganisms, and, therefore, washout of microorganisms occurs. Other limitations for this design are the mass-transfer resistance between the bulk liquid and the cells inside the particles, as well as the short stability and activity of the cells.

Another new design, reported by McCleaf and Shroeder (1995), is a bench-scale membrane-immobilized biofilm reactor (not included in Table 4). This system consisted of a two-chambered reactor separated by a microporous membrane. The biofilm was immobilized on the membrane on the side of the chamber containing a methanol solution. The nitrate-contaminated water was in the other chamber. Batch experiments showed a denitrification rate of 5.8 g NO_3^--N/m^2-d of membrane surface area. Although the methanol source was separated from the water by the biofilm and the membrane, slight contamination of methanol in the treated water was found. Further continuous-operation studies are necessary to investigate the stability of this technology.

The prior studies using heterotrophic denitrification prove that regulatorily acceptable concentrations of NO_3^--N and trace levels of NO_2^--N can be achieved with a range of process types and organic electron donors. The operating strategies chosen gave significant concentrations of organic material in the effluent, and this required major post-treatment efforts to produce a biologically stable water and for disinfection. Whether or not heterotrophic denitrification can be operated without having significant effluent concentrations of organic substrates and NO_2^- is unknown.

3.2 Previous experiences with autohydrogenotrophic denitrification

Limited information from previous studies on autohydrogenotrophic denitrification of drinking water, mostly from Europe, is summarized in Table 5. Kurt et al. (1987) studied autotrophic denitrification in a cone-shaped fluidized sand-bed reactor using a mixed culture. The cone-shape caused a reduction of linear flow rate from the bottom to the top of the reactor. This velocity gradient resulted in a density gradient of biofilm-sand particles, with the largest biofilm particles at the top and relatively clean sand at the bottom. Batch experiments in this study exhibited nitrite accumulation, but continuous experiments resulted in complete N removal, provided that the residence time was sufficient. For complete denitrification of water containing 25 mg NO_3^--N/l, a residence time of 4.5 hr was required. The optimum pH was 7.5. The dynamic effects of flow variation observed during continuous operation indicated that the process could best be operated as a multistage process.

Tuisel et al. (1989) investigated the kinetics of autohydrogenotrophic denitrification using a fluidized-bed biofilm reactor with sand carriers. In batch experiments, the NO_3^- content in the raw water, 29.7 mg NO_3^--N/l, was reduced to nondetectable NO_3^--N after 5 hrs. The pH was controlled at 7 by phosphoric acid addition. When phosphate was not added to the raw water, the denitrification efficiency decreased by nearly 70%. When the operational temperature decreased from 18 to 12 °C,

Table 5. Previous studies in autohydrogenotrophic denitrification of drinking water.

Parameter	Kurt *et al.*, 1987	Tuisel *et al.*, 1989[c]	Dries *et al.*, 1988	Gros *et al.*, 1988	Membran study
Media type	sand	sand	polyurethane sponges	Mellapack[a]	Tri-Packs
Diameter, mm	0.3	not described	10	-	No. 1/2 (1")
Inoculum microorganism	Mixed culture	not described	*A. eutrophus*	not described	not described
Bed type	Fluidized, Upflow	Fluidized, Upflow	Fixed, Downflow[b]	Fixed, Upflow	Fixed, upflow
Specific surface area, m^{-1}	740	not determinable	230	not determinable	139.5
H_2-supply system	Gas sparging to recyle line	H_2 saturator in recyle line	Contact with static H_2 phase in recyle line	Direct contact	H_2 dissolution unit in recycle line
Influent NO_3^--N concentration, mg N/l	10-20	24	15 or 50	18	6.3-150
Effluent concentrations					
NO_3^--N, mg N/l	<0.1	<0.1	<0.1	<1	0.03-40[d]
NO_2^--N, mg N/l	<0.1	<0.1	<0.1	<0.01	
H_2, mg/l	1.1-1.4	not determined	1.1	not determined	not determined[e]
NO_3^--N elimination rate, $gm^{-3}d^{-1}$	552 w/ 4.5 hrs LRT for complete denitrification	506, max. rate from batch studies	250 w/ 1.4 hrs liquid residence time (LRT)	250 w/ 1-2 hrs LRT	130-2160
H_2 loading rate, $gCODm^{-3}d^{-1}$	1,900[g]	1,730	860	860	450-7,400
H_2 surface loading (J), $gCODm^{-2}d^{-1}$	0.96-1.2	not determinable	1.28	not determinable	3.2-52.8[f]
J/J_R	0.013-0.016	not determinable	0.017	not determinable	not determinable

[a] Mellapack is a 3-dimensional corrugated-structured media made of polypropylene with surface area of 250-500 m^2/m^3.
[b] Dual-column system with the first and half of the second column being the denitrifying section. The upper part of the second column is for nitrification (O_2 sparged) in which excess nitrite is removed.
[c] Only the results from start-up period and batch experiments are shown.
[d] The effluent N concentration includes both NO_3^- and NO_2^-. The results presented are from short term nonsteady-state experiments.
[e] H_2 concentration after the gas dissolution device in recycle line is provided (0.09-1.15 mg H_2/l), but effluent H_2 concentration is not measured.
[f] The surface H_2 flux is based on effluent H_2 concentration calculated from stoichiometry proportional to NO_3^- removal.
[g] All H_2 loading rates are computed based on the H_2/N ratio of 0.43 g H_2/gN.

the rate of denitrification declined by 34%, with the maximum denitrification rate being 0.5 kg NO_3^--N/m^3-d at 18 °C and 0.33 kg NO_3^--N/m^3-d at 12 °C.

Dries et al. (1988) used a dual-column reactor, which is comprised of a downflow fixed bed for the first column and an upflow column for the second bed, to study the performance of autohydrogenotrophic denitrification. The H_2 was supplied to the reactor by direct bubbling of H_2 gas in the downflow column. In this system, the top half of the second column was aerated for nitrification to convert the residual nitrite to nitrate. Three types of polyurethane sponge matrices were used as the biofilm carrier. For water containing 15 mg NO_3^--N/l, removal rates of 0.5 kg NO_3^--N/ m^3-d were reached at 20 °C. The percentage of H_2 consumption amounted to 50-55%.

All the studies in Table 5 were lab-based except for Gros et al. (1988), who demonstrated the performance of the first commercial-scale biological drinking-water denitrification plant utilizing hydrogen at Rasseln near Monchengladbach, Germany. Named the Denitropur process, this plant consists of nine upflow, fixed-bed denitrification reactors in a series and packed with Mellapack, which is a mixing element (made of polypropylene) with a 3-dimensional corrugated structure. The raw water (groundwater) was saturated with hydrogen under overpressure and enriched with phosphate and carbon dioxide. After denitrification, the water was aerated and filtered on a two-layer filter. Disinfection was ensured by means of UV radiation. The 50 m^3/hr facility lowered the nitrate concentration from 17 to less than 1 mg/l of NO_3^--N within a residence time of water in the reactors of about 1 hr.

The first four experiences reviewed in Table 5 have the same H_2 provision scheme, i.e., hydrogen gas sparging, either in a separated hydrogen saturation tank (Kurt et al., 1987; Tuisel et al., 1989; Gros et al., 1988) or directly to the reactor (Dries et al., 1988). This kind of scheme has two disadvantages. First, H_2-gas sparging of the system always results in saturation or close to saturation of dissolved H_2 (1.6 mg/l at 20 °C). Although the high H_2 concentration usually allows a low nitrate concentration (perhaps forcing

nitrate to be the limiting substrate), a significant amount of H_2 is lost with the effluent stream. This "wastes" electron donor and could create an explosive atmosphere. Since partial removal of NO_3^- is allowed (i.e., the effluent concentration of NO_3^- simply needs to be below the standard), a denitrification process with H_2 limitation should be regulatorily viable and economically favorable. H_2 limitation is achieved with a low H_2 concentration (Rittmann, 1995). Second, direct H_2 gas sparging in a denitrifying reactor (i.e., to dissolve H_2 gas into the bulk liquid) can facilitate stripping of NO and N_2O out of the liquid phase and may lead to overproduction of NO and N_2O due to the competition from stripping loss of NO and N_2O (Schulthess et al., 1995; Goretski et al., 1990). Due to the toxic or undesirable effect of NO and N_2O (a green-house gas), this situation should be avoided.

Supported by a Small Business Administration grant, Membran Corporation conducted a preliminary study using an upflow, fixed-bed biofilm reactor to investigate the feasibility of denitrification with bubbleless H_2. The biofilm in the reactor was colonized on Jaeger Tri-Packs® No. 1/2 (nominal size 1 inch). The hydrogen supply was provided through a Membran Bubbleless Membrane Gas-transfer system, which is essentially a bundle of hollow, gas-permeable membrane fibers enclosed in a standard water pipe. The denitrifying system was first operated to provide a steady-state biofilm with an approximate thickness of 1 mm. Then, series of nonsteady-state, short-term experiments (20-30 min) were conducted by varying feed NO_3^- concentration ranging from 6.3 to 150 mg N/l. The influent H_2 concentrations were between 0.1 and 1.1 mg/l. Effluent N concentration ($NO_3^- + NO_2^-$) ranged from 0.01 to 40 mg N/l. By controlling the NO_3^- and H_2 concentrations, the nitrogen flux was modulated about 15 fold (929 to 15,490 mg N/m^2-d).

The results from Membran's study showed that the system was capable of producing an effluent with a N concentration below 0.1 mg/l when the effluent H_2 concentration was high (>0.2 mg/l). Another important observation was that partial removal of NO_3^- was possible when the effluent H_2 concentration was driven below

approximately 0.16 mg/l (H_2 as the limiting substrate). Therefore, the hydrogen concentration in the treated water was minimized by keeping hydrogen as the limiting substrate while attaining nitrate concentration in a regulatorily acceptable level.

One other scheme (not included in Table 5), demonstrated by Sakakibara and Kuroda (1993) and Sakakibara et al. (1994a), is a biofilm-electrode reactor in which autotrophic denitrifying microorganisms are immobilized on the surface of the cathode as a biofilm. Hydrogen is generated by applying an electric current to the reactor to support denitrification. An electric energy of 0.22 kWh/m^3 (2.2 V) to the reactor can achieve a nitrate removal of approximately 10 mg N/l. However, the stability and applicability of this system demand further investigations.

Although these studies have demonstrated that a significant removal of nitrate without nitrite accumulation can be achieved using H_2 as the electron donor, their empirical design provides very limited information regarding substrate utilization and biofilm kinetics. For instance, none of the above studies provides the biomass concentration in the effluent, which is essential to the understanding of biofilm kinetics. In most cases, the concentration of the electron donor was not measured. Despite some severe limitations, this information shows that autohydrogenotrophic denitrification can be a clean and efficient alternative for drinking water denitrification. However, further investigation on the biofilm kinetics to gain extensive insight into what controls the performance of autohydrogenotrophic denitrification is necessary.

Chapter 4. Design Criteria

4.1 Biofilm systems and substrate utilization kinetics

A biofilm is an aggregation of microbial cells, in association with extracellular polymers excreted by these cells, immobilized on a substratum (i.e., the surface of the support media). The thickness of biofilms can be less than a monolayer of cells or as thick as 300-400 mm, as in algal mats (Characklis and Marshall, 1990). A typical engineering biofilm system consists of a substratum (such as a sand particle), bulk liquid, biofilm, and, sometimes, gas as in a three-phase biofilm filter. The substrates and nutrients in the bulk liquid must be transferred into the cell matrix in order to be utilized for cell growth. Two major mass-transfer processes usually are considered: the interfacial transfer between the bulk liquid and the biofilm surface, and the transport of the substrates within the biofilm, in which the substrate-utilization reactions and biomass accumulation occur simultaneously. Under steady-state conditions, which rapidly develop, the rate of substrate transfer into the biofilm is the same as the rate of substrate consumption inside the biofilm.

In general, the biofilm is modeled as a homogeneous matrix attached to a flat surface. Substrate concentration changes occur only in the direction perpendicular to the surface (Rittmann and McCarty, 1980). Figure 1 is a graphic presentation of substrate concentration profiles of such a biofilm system. S, S_s, S_f, and S_w represent the substrate concentration (M_sL^{-3}) in the bulk liquid, diffusion layer-biofilm interface, biofilm, and the biofilm-support surface interface, respectively. Three different types of concentration profiles are shown in Figure 1, i.e., fully penetrated, shallow, and deep biofilms. A fully penetrated biofilm is one that has the same substrate concentration S along the whole profile ($S= S_s = S_f = S_w$). A deep biofilm has a S_f decreasing to zero as it approaches the support surface. Other cases, in which $0<S_f<S_s$, are called shallow biofilms.

The concentration gradient between the bulk liquid and the biofilm surface is caused by the mass-transfer resistance through the diffusion layer. Therefore, the flux across the diffusion layer can be expressed by the Fick's first law,

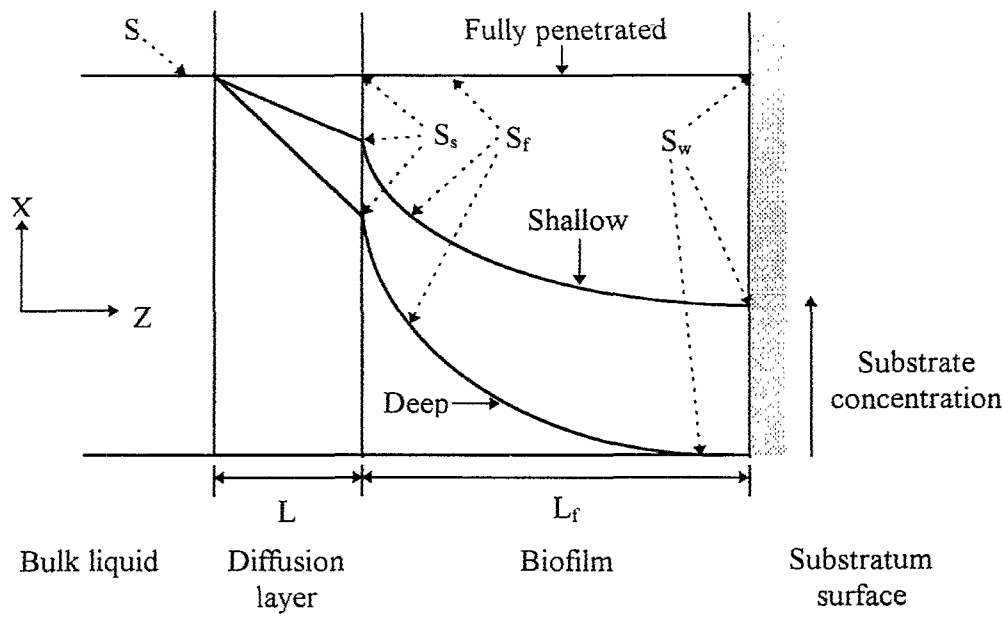

Figure 1. Graphic presentation of a biofilm system and the substrate concentration profiles.

$$J = -D\frac{dS}{dz} = D\frac{S - S_s}{L} \tag{4-1}$$

where J is the flux across the diffusion layer ($M_sL^{-2}T^{-1}$), D is the molecular diffusion coefficient of the substrate in the liquid (L^2T^{-1}), and L is the thickness of the diffusion layer (L). When the substrate concentration reaches a steady state, the substrate that diffuses into the biofilm is balanced by the utilization of that substrate. This steady-state mass balance can be described mathematically as

$$0 = D_f\frac{\partial^2 S_f}{\partial z^2} + r_u \tag{4-2}$$

$$r_u = -q_m\frac{S_f}{K_s + S_f}X_f \tag{4-3}$$

where D_f is the diffusion coefficient of the substrate in the biofilm (L^2T^{-1}), q_m is the maximum specific substrate utilization rate ($M_sM_x^{-1}T^{-1}$), K_s is the half-maximum-rate substrate concentration (M_sL^{-3}), and X_f is the biomass density of the biofilm (M_xL^{-3}). The first term on the right side of equation (4-2) is the substrate diffusion in the biofilm expressed by Fick's second law. The second term (r_u) is the specific substrate utilization rate ($M_sL^{-3}T^{-1}$). r_u is often expressed by a Monod type utilization kinetics, as shown in equation (4-3).

A biofilm is at steady state if the net growth rate of the biofilm per unit surface area is equal to the rate of biofilm loss due to cell decay and biofilm detachment. This relationship can be written as (Sáez and Rittmann, 1988, 1992)

$$JY = X_f L_f b' \tag{4-4}$$

where Y is the true yield ($M_xM_s^{-1}$) and b' is the overall specific biofilm loss rate (T^{-1}), which includes the endogenous cell decay rate (b) and the biofilm detachment rate (b_{det}). To sustain a steady-state biofilm, a minimum substrate concentration, S_{min}, exists and is described as

$$S_{\min} = K_s \frac{b'}{Yq_m - b'} \tag{4-5}$$

If the concentration is below S_{min}, the loss of biofilm exceeds the cell growth, and, therefore, the thickness of biofilm will decrease or no biofilm will be formed (Rittmann and McCarty, 1980a). A pseudoanalytical solution to this biofilm model was developed by Sáez and Rittmann (1988) and further improved by Sáez and Rittmann (1992).

4.2 The normalized loading curves

Based on the pseudoanalytical solution, Heath et al. (1990) and Wirtel et al. (1992) developed a design technique for biofilm processes using normalized loading curves (NLCs). The NLCs define the performance of a steady-state biofilm reactor with four fundamental parameters, i.e., S_{min}, S^*_{min}, J_R, and K^*. S^*_{min} and K^* are dimensionless form of S_{min} ($S^*_{min} = S_{min}/K_s$) and mass transport $K^* = D/L(K_s/(q_m X_f D_f))^{0.5}$. S^*_{min} represents the growth potential of the microorganisms. A high growth potential is represented by a S^*_{min} value much less than 1, whereas a S^*_{min} value near to or greater than 1 indicates that the growth rate is only slightly greater than the biofilm loss rate. K^* normalizes the external mass-transfer resistance by the film reaction potential; a value of K^* much greater than 1 indicates the mass-transfer resistance is insignificant. J_R is the reference substrate flux that defines the minimum flux capable of supporting a deep steady-state biofilm. J_R can be computed from the relationship of J_R^*/S_{min}^* versus S_{min}^*, where $J_R = J_R^*(K_s q_m X_f D_f)^{0.5}$. This relationship was graphically presented by Cannon (1991) and Sáez and Rittmann (1992) and is shown in Figure 2. Fast reaction kinetics or slow internal diffusion reduce J_R, making it easier for the biofilm to be deep, or its kinetics controlled by mass-transport processes.

Figure 3 and 4 gives two examples of NLCs for denitrification. Their significance to the design of drinking water treatment is discussed in the next section. As shown in either figure, when the substrate flux (J) is low in comparison with J_R, S is insensitive to

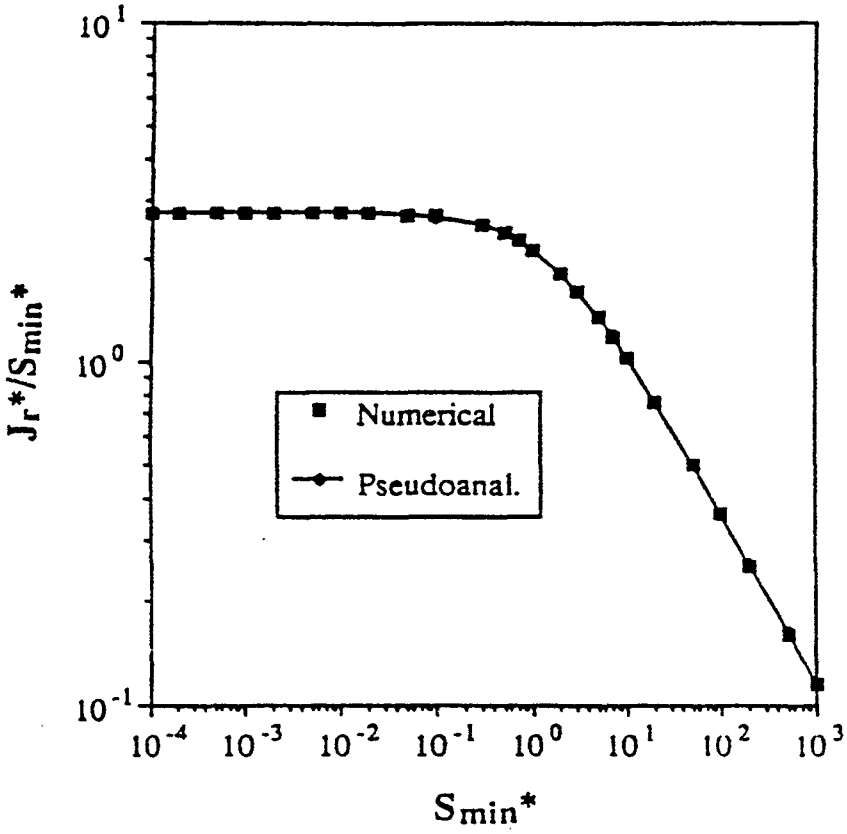

Figure 2. The curve of J_R^*/S^*_{min} versus S^*_{min} generated from the pseudoanalytical solution (after Sáez and Rittmann, 1992).

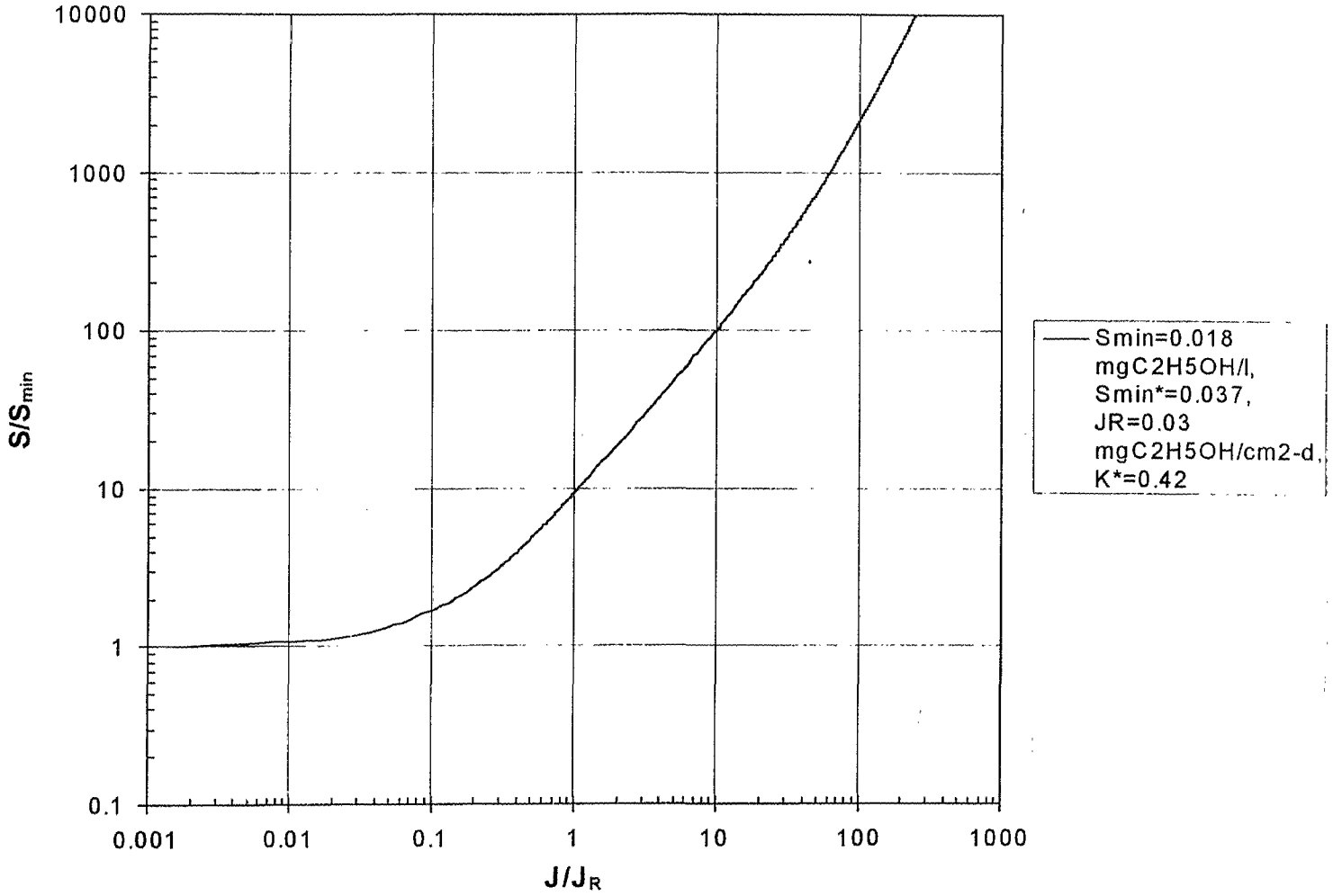

Figure 3. The normalized loading curve for designing the heterotrophic denitrification system using C_2H_5OH; $q_{m,C2H5OH}$ =5.65 mg C_2H_5OH/mg cells-d, $K_{s,C2H5OH}$ =0.48 mg/l, X_f=40 mg/cm^3, b′= 0.1 d^{-1}, Y=0. 5 mg biomass/mg C_2H_5OH, D=1.1 cm^2/d, D_f=0.86 cm^2/d, and L=0.004 cm.

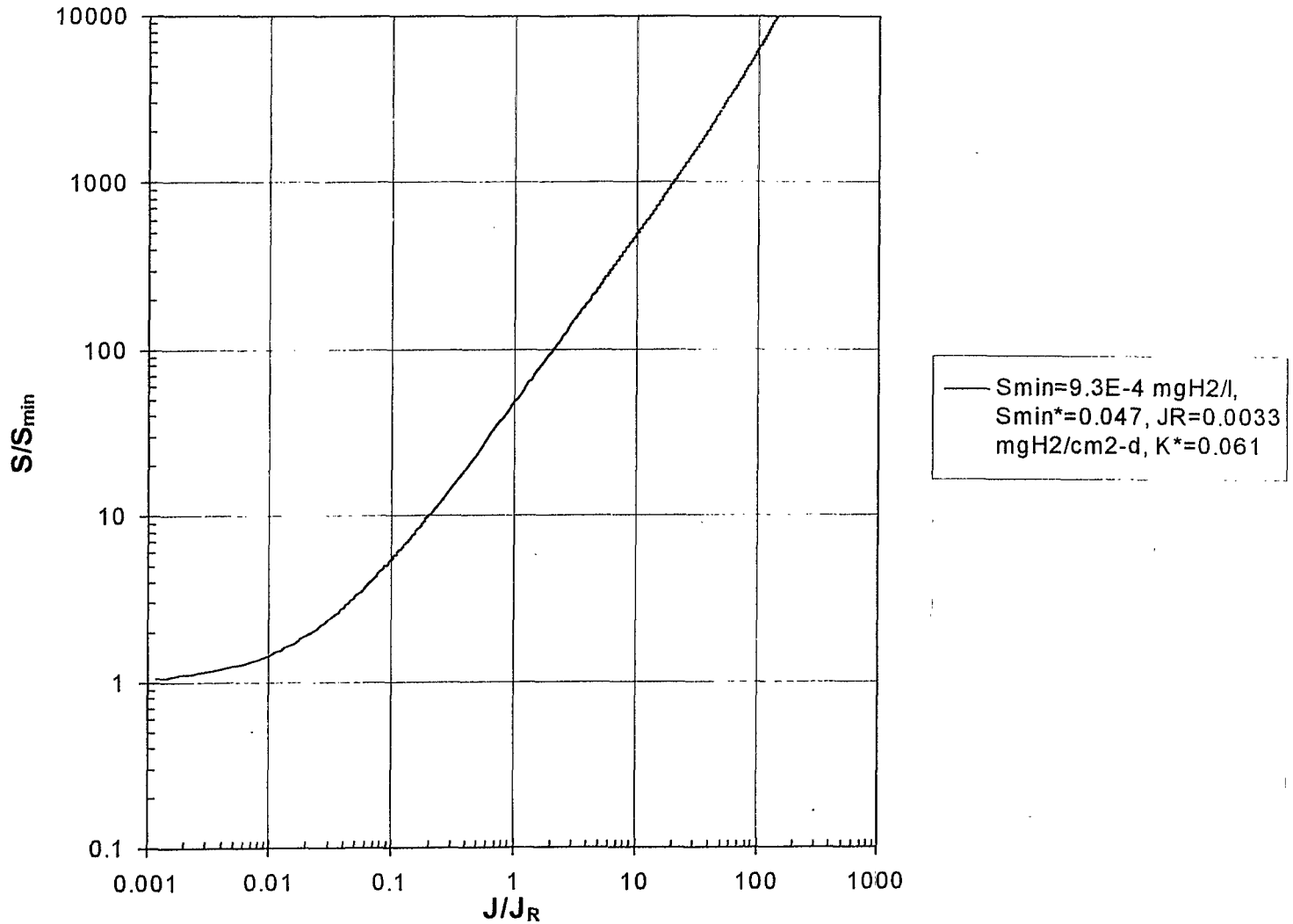

Figure 4. The normalized loading curve for designing the autohydrogenotrophic denitrification system; $q_{m,H2}$=2.65 mgH_2/mg cells-d, $K_{s,H2}$=0.002 mg/l, X_f=40 mg/cm^3, b′= 0.1 d^{-1}, Y=0.85 mg biomass/mg H_2, D=3.9 cm^2/d, D_f=3.1 cm^2/d, and L=0.005 cm.

changes in J. This is the low loading region, and S in this region is close to S_{min}. Substrate flux is mainly controlled by biomass accumulation in the low-load region. When J is higher than J_R, however, a slight increase in J can dramatically increase S, as illustrated in the region where J/J_R is greater than about 1. In this high loading region, the substrate flux is strongly controlled by the interaction between substrate utilization and transport to and in the biofilm.

4.3 Design procedure

The basis for the design of a biofilm reactor using the NLC technique is the mass-balance relationship between the steady-state substrate flux (J) and the steady-state substrate concentration (S)

$$J = \frac{Q(S^o - S)}{aV} \tag{4-6}$$

where

Q: the volumetric flow rate of the influent (L^3T^{-1}),

V: volume of the biofilm reactor (L^3),

S^o: the influent substrate concentration (M_sL^{-3}),

a: the specific surface area of the biofilm carrier (L^{-1}).

When designing a biofilm reactor, S^o, S, and Q usually are known. The a value is known when the biofilm carrier is chosen. Therefore, the volume of the biofilm reactor can be calculated by

$$V = \frac{Q(S^o - S)}{aJ} \tag{4-7}$$

when J is estimated from the proper NLC. That NLC is identified when the parameters for the substrate limiting the rate of denitrification (q_m, K_s), the biofilm (b', X_f), and the mass-transport properties of the substrate (D, D_f, L) are known. From these parameters, S_{min}, S_{min}^*, K^*, and J_R can be computed according to the procedure in the previous section.

S_{min}^* and K^* define what curve to choose, while J_R and S_{min} normalize the J and S scales (Wirtel et al., 1992). The performance of the reactor system is determined by the simultaneous solution of Eq. 4-7 and the S vs. J relationship of the NLC.

Two examples for the design of a denitrifying biofilm reactor using either ethanol or hydrogen are given here. The biofilm reactor is a fluidized-bed reactor using sand particles with 1-mm diameter and a specific surface area of 2,400 m^{-1} (60% expansion). The design flow rate is 960 m^3/d. The process is to reduce the nitrate concentration from 15 to 2 mg N/l. The design concentration of either ethanol or hydrogen in the reactor is 0.8 mg OD/l in the first example, which represents an ethanol concentration of 0.4 mg C_2H_5OH/l and a hydrogen concentration of 0.1 mg H_2/l. The 0.8 mg OD/l concentration gives a treated water with a moderate level of biological instability. It should be noted that the ethanol will remain in solution unless biodegraded in a post-treatment step, while the hydrogen gas will evolve if the water is exposed to an open surface.

The required influent ethanol and hydrogen concentrations are computed from the stoichiometric consumption ratio (α) between the electron-donor substrate and nitrogen shown in Table 3, which gives a C_2H_5OH/N ratio of 2.27 g ethanol/g N and a H_2/N ratio of 0.43 g H_2/g N. The formula for computing the influent electron donor substrate concentrations is

$$S_d^o = (S_N^o - S_N)\alpha + S_d \tag{4-8}$$

where

S^o_d: influent electron donor concentration (MsL^{-3}),

S^o_N: influent nitrate nitrogen concentration (MsL^{-3}),

S_N: steady-state nitrate nitrogen concentration (MsL^{-3}),

S_d: steady-state electron-donor substrate concentration (MsL^{-3}).

The computed ethanol and hydrogen concentrations are 30 mg/l and 5.7 mg/l, respectively, for the influent.

Since the fluidized-bed reactor is usually accompanied with a high recirculation flow, the reactor is close to a completely-mixed regime, and, therefore, the substrate concentration can be assumed uniform throughout the reactor. Table 6 summarizes the typical design and kinetic parameters. Computed values for S_{min}, S_{min}^*, K^*, and J_R are shown in Table 6. Then, the correct NLC for ethanol and hydrogen can be found according to the respective S_{min}^* and K^*. Figures 3 and 4 represents the NLCs for ethanol and hydrogen, respectively. Then, J and the volume of the reactor (V) can be found according the following procedure.

Ethanol

- S/S_{min} is calculated as (0.4 mg C_2H_5OH/l)/(0.018 mg C_2H_5OH/l)=22.2.
- J/J_R is determined from Figure 3 as 2.3.
- J is calculated as 2.3x(0.03 mg C_2H_5OH/cm^2-d)=0.069 mg C_2H_5OH/cm^2-d.
- The volume of the reactor can calculated using Eq. 4-7

$$V = \frac{960\, m^3/d \times (30-0.4)\, mg/l \times 10^3\, l/m^3}{2400 m^{-1} \times 0.069\, mg/cm^2 \cdot d \times 10^4\, cm^2/m^2} = 17.2 m^3.$$

Hydrogen

- S/S_{min} is calculated as (0.1 mg H_2/l)/(9.3x10^{-5} mg H_2/l)=1075.
- J/J_R is determined from Figure 4 as 21.3.
- J is calculated as 21.3x(0.0033 mg H_2/cm^2-d)=0.07 mg H_2/cm^2-d.
- The volume of the reactor can calculated using Eq. 4-7

$$V = \frac{960\, m^3/d \times (5.7-0.1)\, mg/l \times 10^3\, l/m^3}{2400 m^{-1} \times 0.07\, mg/cm^2 \cdot d \times 10^4\, cm^2/m^2} = 3.2 m^3.$$

Table 6. Design parameters for a denitrifying fluidized-bed biofilm reactor using ethanol or hydrogen as the electron-donor substrate.

Design parameters	Ethanol	Hydrogen
K_s (g/m^3)	0.48	0.002
q_m (g/gcells-day)	5.65	2.65
X_f(gcells/m^3)	40000	40000
D_f(m^2/day)	0.000086	0.00031
D (m^2/day)	0.00011	0.00039
Y (gcells/g)	0.5	0.85
L (m)	0.00004	0.00005
b' (day-1)	0.1	0.1
S_{min} (g/m^3)=$S^*_{min}xK_s$	0.018	9.3E-05
S^*_{min}=b'/(Yq_m-b')	0.037	0.047
K*=D/L*(K/qmXfDf)$^{0.5}$	0.42	0.06
J_R (g/m^2/day)	0.31	0.033
J^*_R	0.1	0.13

The calculated volumes of the denitrifying fluidized-bed reactor for using ethanol and hydrogen are 17.2 and 3.2 m^3, respectively. This gives empty-bed liquid detention times of 26 and 4.8 minutes, respectively, and NO_3^--N elimination rates of 726 and 3,900 gN/m^3-d, respectively. This example demonstrates that, because of the difference in the intrinsic substrate utilization kinetics, the necessary reactor volume for using hydrogen can be substantially less than that when ethanol is used and when the same effluent oxygen-demand concentration is used. If the ethanol system were to have the same 3.2-m^3 volume as the hydrogen system, its ethanol flux would need to be increased to 0.37 mg C_2H_5OH/cm^2-d, and this would force the effluent ethanol concentration to rise to 2.28 mg C_2H_5OH/l, or 4.8 mg OD/l. The result would be a water with very great biological instability.

For a second example, the effluent concentration of the electron donor substrate is set at 0.03 mg OD/l, which gives effluent concentrations of 0.014 mg C_2H_5OH/l and 0.004 mg H_2/l. This 0.03 mg OD/l is low and represents a S/S_{min} value of 0.8 for ethanol. From the biofilm kinetics principle discussed in section 4.1, a steady-state biofilm cannot be sustained at a substrate concentration below the S_{min} (S/S_{min} <1), and, therefore, steady-state denitrification is not possible with the given ethanol concentration. The following computations show the design using hydrogen as the electron-donor substrate.

Hydrogen

- S/S_{min} is calculated as (0.004 mg H_2/l)/(9.3×10^{-5} mg H_2/l)=43.
- J/J_R is determined from Figure 4 as 0.9.
- J is calculated as 0.9x(0.0033 mg H_2/cm^2-d)=0.003 mg H_2/cm^2-d.
- The volume of the reactor can calculated using Eq. 4-7

$$V = \frac{960\,m^3/d \times (5.6 - 0.004)\,mg/l \times 10^3\,l/m^3}{2400m^{-1} \times 0.003\,mg/cm^2 \cdot d \times 10^4\,cm^2/m^2} = 74.6m^3.$$

The computed volume for the fluidized-bed denitrifying reactor using as the electron donor is 74.6 m^3 when the effluent hydrogen concentration is only 0.004 mg H_2/l (0.03 mg OD/l). This gives a volumetric loading of 167 g N/m^3-d and an empty-bed detention time of 112 minutes.

The above examples show that the normalized-loading curve technique can be easily employed as a design tool for biofilm systems. However, it is important to point out that the substrate utilization kinetics, as well as the mass-transfer parameters, sensitively affect the process design. Many of the parameters used in Table 6 are generic or assumed. Therefore, results from lab-scale or pilot-scale studies that accurately measure the kinetic parameters and investigate the hydrodynamic behavior of the biofilm particles are extremely valuable for the design of a good full-scale system.

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APPENDIX C
BUDGET EXPLANATION

Section 7 provides the detailed budget for the two-year project. The total amount requested from AWWARF is $274,960. Northwestern University, the three participating utilities, and Montgomery Watson provide an *in-kind* contribution of $92,083 making the budget total $367,043.

All cost items are in accord with AWWARF guidelines. A few notes on specific items include:

1. Maintenance is for analytical equipment, particularly the TOC analyzer and the gas chromatograph, and the H_2 analyzer.
2. Travel is for two persons to attend a national conference and for two investigator's meetings.
3. Northwestern contributes 80 percent of the student's tuition, which is shown as an *in-kind* contribution. The student pays the remaining 20 percent.
4. Salaries escalate at 4 percent per year.
5. The indirect cost rate is 48 percent, which is the government-negotiated rate for Northwestern University.
6. Northwestern University charges indirect costs only on the first $25,000 of the subcontract to Montgomery Watson.
7. Northwestern's *in-kind* contribution consists of 42% of Dr. Rittmann's time for project supervision and the cost of equipment, supplies, and fabrication of the H2-membrane biofilm reactor.
8. The three utilities' in-kind contribution are for analytical work performed in their laboratories. The letters in Appendix D and the In-Kind Support Work Sheet itemize the contributions.
9. The subcontract budget for Montgomery Watson is given on the next page. Montgomery Watson is also providing in-kind contributions, in the form of some of Dr. Najm's time.

Application of Bioreactor Systems to Low-Concentration Perchlorate-Contaminated Water (RFP 2530)

Montgomery Watson's Budget

Budget Estimate Form						
LABOR COST						
Name	**# of Hours**	**Percent Commitment (of 24 mo.)**	**Hourly Rate**	**TOTAL COST**	**NWU Cost**	**In-Kind Contribution**
Issam Najm	347	9%	$145	$50,270	$47,270	$3,000
Lina Boulos	342	9%	$70	$23,940	$23,940	
Administrator	113	3%	$48	$5,424	$5,424	
SUBTOTAL LABOR COST =				**$79,634**	**$76,634**	**$3,000**
OTHER DIRECT COSTS (ODCs)						
Item				**TOTAL COST**	**NWU Cost**	**In-Kind Contribution**
Travel & Lodging (Project Workshops & PAC Meetings)				$3,150	$3,150	
Analytical Services				$24,150	$24,150	
Associated Project Cost (Telecomm, reproduction, postage...)				$5,966	$5,966	
SUBTOTAL OTHER DIRECT COSTS =				**$33,266**	**$33,266**	
TOTAL BUDGETED COST =				**$112,900**	**$109,900**	**$3,000**

APPENDIX D
LETTERS OF COMMITMENT

CITY OF RIVERSIDE

"People Serving People"

April 30, 1998

Issam Najm
Montgomery Watson
555 East Walnut Street
Pasadena, CA 91101

Dear Mr. Najm:

AWWARF RFP 2530:
Application of Bioreactor Systems to Low-Concentration Perchlorate-Contaminated Water

The purpose of this letter is to express the interest and support of the City of Riverside, California in the above named research project. We would welcome the opportunity to provide water quality data for the study to the Northwestern University-Montgomery Watson team.

As an estimate, the approximately in-kind value of this participation is $2,000 for providing historical and most recent available water quality data for your research project.

We look forward to working with you on this project. If you have any further questions please contact Zahra Panahi at (909) 782-5612.

Very truly yours,

for Bill D. Carnahan
Public Utilities Director

cc: Dieter P. Wirtzfeld
Eileen Teichert
Zahra Panahi
Dan Randall

PUBLIC UTILITIES DEPARTMENT
3900 MAIN STREET • RIVERSIDE, CALIFORNIA 92522
WATER ENGINEERING DIVISION • (909) 782-5285

MainSanGabrielBasin
WATERMASTER

April 27, 1998

Issam Najm, Ph.D., P.E.
Montgomery Watson
555 East Walnut Street
Pasadena, CA 91101

Subject: AWWARF Perchlorate Treatment Studies

Dear Dr. Najm:

The Main San Gabriel Basin Watermaster is very interested in joining your project team in your submittal for the above-referenced AWWARF-sponsored project. Watermaster's proposed participation and contribution is summarized in the attached sheet entitled "Proposed Participation by Main San Gabriel Basin Watermaster in Various Treatability Studies for Perchlorate-Containing Water." Please note that this proposal is a non-exclusive proposal, and Watermaster may join project teams formed by other interested parties.

If you have any questions or desire additional information, please contact me or Rick Sase at (626) 815-1300.

Sincerely,

MAIN SAN GABRIEL BASIN WATERMASTER

Carol Williams
Executive Officer

Attachment

725 North Azusa Avenue • Azusa, California 91702 • Telephone (818) 815-1300 • Fax (818) 815-1303
http://www.watermaster.org

Printed on Recycled Paper

Proposed Participation
by
MAIN SAN GABRIEL BASIN WATERMASTER
in
Various Treatability Studies for Perchlorate-Containing Water

The Main San Gabriel Basin Watermaster, a court-appointed agency, is responsible for the efficient management of the quantity and quality of the Basin's groundwater and the administration of the Judgment which established water rights. Consequently, Watermaster often performs or administers projects which affect the water producers in order to preserve and protect the primary source of water for over 1,000,000 residents in the San Gabriel Valley in the eastern portion of Los Angeles County, California.

After the development of a testing method in 1997, perchlorate was found to be a contaminant affecting the Basin's groundwater supply. Several potable water supply wells in the Basin were affected, including the shutdown of three wells which were the sole water supply source for La Puente Valley County Water District. In addition, the implementation of USEPA's Baldwin Park Operable Unit, a Superfund cleanup project, has been suspended until the perchlorate contamination problem is resolved.

Due to the urgency, Watermaster has responded very aggressively to find a technically and economically feasible solution to perchlorate contamination. Watermaster allocated $300,000 of its own funds to perform basinwide testing and vulnerability studies and to research and develop perchlorate treatability methods. Because of the complexities of the problem, a highly-qualified special consultant, Michael J. McGuire, Ph.D., was retained to assist Watermaster in overseeing the various projects and activities. In addition, the San Gabriel Perchlorate Coordinating Team was formed as a forum to exchange ideas and information with water agencies/companies, governmental/regulating agencies, consultants, various industries and businesses and other parties affected by perchlorate contamination in Southern California. As a result, Watermaster has reviewed several screening studies, has conducted several investigations and has gained significant firsthand experience in perchlorate contamination issues/technologies.

To determine the best solution in an economical manner, Watermaster proposes to join your project team and provide "in-kind" services during the Phase I, Bench-Scale Laboratory Testing. The "in-kind" services will include (a) the exchange of current data and information on appropriate technologies, (b) assistance in selecting water supply sources which will contain acceptable levels of other chemical constituents, (c) coordination and collection of groundwater samples from selected wells for bench-scale tests, (d) assistance in obtaining any necessary NPDES permits, (e) collection and delivery of water samples to local laboratories, including the performance of a limited number of chemical analyses and (f) technical review of proposed testing procedures and all draft project reports. The level of Watermaster's "in-kind" contribution is estimated at and shall not exceed $10,000. Watermaster's contribution to Phase II projects, if any, will be determined after the results of Phase I are obtained and analyzed.

Administrative Office
1001 S. Valley View Blvd.
Las Vegas, Nevada 89153
Telephone: (702) 258-3939
Fax: (702) 258-8268

Project Office
1900 E. Flamingo, Ste. 170
Las Vegas, Nevada 89119
Telephone: (702) 862-3400
Fax: (702) 862-3470

Southern Nevada Water System
245 Lakeshore Road
Boulder City, NV 89005
Telephone: (702) 564-7697
Fax: (702) 564-7922

SOUTHERN NEVADA
WATER AUTHORITY

April 30, 1998

Issam Najm
Montgomery Watson
555 East Walnut Street
Pasadena, CA 91101

Re: Participation in the AWWARF Project on the Application of Bioreactor Systems to Low-Concentration Perchlorate-Contaminated Water (RFP 2530)

Dear Issam:

The Southern Nevada Water Authority is very interested in joining the Northwestern University-Montgomery Watson team in your submittal for the AWWARF-sponsored project titled: "Application of Bioreactor Systems to Low-Concentration Perchlorate-Contaminated Water (RFP 2530)." Perchlorate in Lake Mead water has had a serious detrimental effect on consumer confidence in our drinking water. We are highly interested in evaluating treatment options for removing perchlorate from the water with the objective of utilizing the product water as a drinking water source. As such, we are interested in evaluating alternative treatment options, one of which is biological treatment.

We understand that the AWWARF project will be divided into two phases, with Phase I focusing on bench-scale laboratory testing, and Phase II focusing on pilot-scale field testing/demonstration. For Phase I, we commit to providing the project team with representative water samples from the water supply to be evaluated for biological perchlorate treatment. The cost of collecting and shipping the samples to the laboratory will be provided as an in-kind contribution to the project. This contribution is estimated at $5000.00.

We hope that you will be successful in your bid, and we look forward to working with you on this interesting and timely project. If you have any questions, please contact me at (702)567-2035.

Sincerely yours,

John L. Frank for DJR

David J. Rexing
Laboratory Manager
Southern Nevada Water System

DJR:cw
By: facsimile

BOARD OF DIRECTORS

Mary J. Kincaid, Chair
County Commissioner

Arnie Adamsen, Vice Chairman
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Paula L. Brown
North Las Vegas Councilman

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Bryan Nix
Boulder City Councilman

Myrna Williams
County Commissioner

Bruce L. Woodbury
County Commissioner

Patricia Mulroy
General Manager

APPENDIX E
RESUMES

BIOGRAPHICAL SKETCH

Bruce E. Rittmann

Northwestern University
Dept. of Civil Engineering
2145 Sheridan Road
Evanston, IL 60208-3190
phone: 847-491-8790
fax.: 847-491-4011
e-mail: b-rittmann@nwu.edu
Date of Birth: 17 November 1950

Professional Interests

Environmental biotechnology: Application of mathematical modeling, geochemistry, kinetics, and molecular biology for studying the interactions among microbiological, chemical, and physical processes in natural and engineered systems. Examples of systems studied include microbially driven fate of radionuclides in DOE co-contamination sites, adaptation of anaerobic communities to chlorinated solvents, acceleration of detoxification reactions by control of intracellular cofactors, biodegradation of petroleum hydrocarbons by microbial mats, water-quality changes in drinking water as it is distributed, biofiltration of gases contaminated with volatile organic contaminants, photobiocatalysis, and use of plasmid transfer to enhance biodegradative capacities of microbial communities.

Educational Activities

- Supervised 12 PhD theses, 9 post-doctoral fellows, 8 visiting scholars, and many undergrads
- Current mentoring: 10 graduate students, 1 post-doctoral fellow, and 3 undergrads.

Employment

- John Evans Professor and Area Coordinator of Environmental Health Engineering and with affilitate appointment in Chemical Engineering, Northwestern University (1992-present)
- Full, Assoc, and Asst. Professor, Dept. of Civil Engineering, University of Illinois at Urbana-Champaign (1980-92)
- Enviromental Engineer, Sverdrup & Parcell and Assoc. (1974-75)

Education

- Ph.D. Environmental Engineering, Stanford University (1979)
- M.S. Environmental Engineering, Washington University (1974)
- B. S. Civil Engineering, Washington University (1974)

Honors and Awards

- Travel Fellowship, Japan Ministry of Education (Monbusho) (1997)
- Fellow, American Association for the Advancement of Sciences (1996)
- A.R.I. Clarke Prize, National Water Research Institute (1994)
- Engineering-Science Award, AEEP (1979 and 1993)
- Montgomery-Watson Award, AEEP (1992 and 1995)
- Walter Huber Research Prize, ASCE (1990)
- Academic Achievement Award, AWWA (1990)
- CH_2M-Hill Award, AEEP (1989 and 1995)
- University Scholar Award, Univ. of Illinois (1987)

- Xerox Faculty Research Award, Univ. of Illinois (1985)
- Presidential Young Investigator Award, NSF (1984)
- Chairman of Committee on In Situ Bioremediation, National Research Council (1992-93)
- Board of Directors, Association of Environmental Engineering Professors (1988-92); President (1990-91)
- Managing Editor, *Biodegradation* (1990-96); Editor-in-Chief (1996-2001)
- Water Science and Technology Board, National Research Council (1991-97); Vice-Chairman (1994-97).
- Chairman of Committee on Intrinsic Remediation, National Research Council (1997-99).

Major Research Accomplishments

Dr. Rittmann is an international leader in the fields of biofilm kinetics, biological treatment of drinking water, detoxification of hazardous organic chemicals, nitrification, the use of molecular techniques to study microbial communities in natural and engineered processes, bioremediation, and mathematical modeling that couples microbial kinetics to geochemical processes. His standing is recognized by the numerous research prizes, by his selection to be a chairman of two National Research Council committees, and Editor-in-Chief of *Biodegradation.*

Significant Publications (total number is 220)

Sáez, P. B. and B. E. Rittmann (1993). Biodegradation kinetics of a mixture containing a primary substrate (phenol) and an inhibitory co-metabolite (4-chlorophenol). Biodegradation 4: 3-23.

Raskin, L., L. K. Poulson, D. R. Noguera, B. E. Rittmann, and D. A. Stahl (1994). Quantification of methanogenic groups in anaerobic biological reactors using oligonucleotide probe hybridizations. Appl. Environ. Microb. 60: 1232-1240.

Teske, A., E. Alm, J. M. Regan, S. Toze, B. E. Rittmann, and D. A. Stahl (1994). Evolutionary relationships among ammonia- and nitrite-oxidizing bacteria. J. Bacteriology 176: 6623-6630.

Rittmann, B. E. (1995). Transformation of organic micropollutants by biological processes. Quality and Treatment of Drinking Water, J. Hrubec, Ed., The Handbook of Environmental Chemistry, Vol. 5B, pp 31-60.

Malmstead, M. J., F. Brockman, A. J. Valocchi, and B. E. Rittmann (1995). Modeling biofilm biodegradation requiring cosubstrates: the quinoline example. Water Sci. Technol. 31(1): 71-84.

Bae, W. and B. E. Rittmann (1995). Accelerating the rate of cometabolic degradations requiring an intracellular electron source--model and biofilm application. Water Sci. Technol. 31(1): 29-39.

Wrenn, B. A. and B. E. Rittmann (1996). Evaluation of a mathematical model for the effects of primary substrates on reductive dehalogenation kinetics. Biodegradation 7: 49-64.

Smets, B. F., B. E. Rittmann, and D. A. Stahl (1996). Quantification of the effect of substrate concentration on the conjugal transfer rate of the TOL plasmid in short-term batch mating experiments. Letters in Applied Microbiology 21: 167-172.

Guschin, D. Y., B. K. Mobarry, D. Proudnikov, D. A. Stahl, B. E. Rittmann, and A. D. Mirzabekov (1997). Oligonucleotide microchips as genesensors for determinative and environmental studies in microbiology. Appl. Environ. Microb. 63: 2397-2402.

Brusseau, G. A., B. E. Rittmann, and D. A. Stahl (1997). Addressing the microbial ecology of marine biofilms. In K. E. Cooksey, ed., Molecular Approaches to the Study of the Oceans, pp. 449 - 470.

Yu, H. and B. E. Rittmann (1997). Predicting bed expansion and phase holdups for three-phase, fluidized-bed reactors with and without biofilm. Water Research 31: 2604-2616.

ISSAM N. NAJM, Ph.D., P.E.
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MONTGOMERY WATSON
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EDUCATION:

Ph.D., Environmental Engineering, University of Illinois at Urbana-Champaign	1990
M.S., Environmental Engineering, University of Illinois at Urbana-Champaign	1987
B.S., Civil Engineering, American University of Beirut, Lebanon	1985

REGISTRATION:

Professional Civil Engineer, State of California. Registration Number C 57496

SUMMARY:

Issam Najm is the manager of Montgomery Watson's Applied Research Department in Pasadena, California. He has extensive experience in bench-scale and pilot-scale process testing and evaluation of water and wastewater treatment processes. He is currently involved in several drinking water treatment projects including ozonation, coagulation, GAC adsorption, and biofiltration processes for the control of disinfection by-products, as well as evaluation and monitoring of distribution system water quality, and treatment of contaminated groundwaters.

EXPERIENCE:

Groundwater Treatment

Dr. Najm served as the project manager on a groundwater treatment project for the US Army Environmental Center. The project focused on evaluating the use of the PEROXONE process (Ozone with Hydrogen Peroxide) for the destruction of trinitrotoluene (TNT), trinitrobenzene (TNB), and other contaminants from a groundwater source.

Dr. Najm served as the treatment process engineer on a groundwater treatment study for the City of Houston, TX. The project involved an assessment of the level of arsenic and radon contamination in the City's groundwater, as well as the evaluation of various treatment processes for the removal of arsenic and radon from the contaminated groundwater.

Dr. Najm was the project engineer on a treatment alternative feasibility study for the treatment of VOC- and Radon-contaminated groundwater using a combination of air-stripping and liquid-phase and gas-phase granular activated carbon (GAC) adsorption. The proejct was conducted for the Metropolitan Water District of Southern California. Bench-scale testing, pilot-scale testing, and mathematical modeling of the process alternatives were conducted to determine the optimum and cost effective process design criteria. The contaminants of concern were volatile organic

chemicals (VOCs) and radon. Pilot-scale testing was conducted to evaluate the adsorption of radon present in the air-stripping off-gas stream onto granular activated carbon.

Water Reclamation

Dr. Najm is currently serving as the project engineer for a water quality improvement project for the Central Basin Municipal Water District, in Southern California, aimed at improving the water quality in the District's reclaimed water distribution system. The first phase of the project includes distribution system monitoring and cleaning. The second phase will include analysis of fluctuations in customer water demand, estimating residence time distribution in the system, and determination of the chlorine decay rate. The final phase of the project will include a feasibility study for the alternatives available for boosting the chlorine residual in the distribution system, as well as a recommendation for a permanent solution.

Corrosion

Dr. Najm served as the technical director of a copper corrosion study at the East Bay Municipal Utility District (EBMUD). Bench-scale and pilot-scale studies were conducted to determine the cause of the formation of blue deposits on the surfaces of in-house plumbing. Further, Dr. Najm currently serves the a member of Project Advisory Committee (PAC) for a copper corrosion project funded by the American Water Works Association Research Foundation (AWWARF). The project is evaluating the effects of various inorganic and organic constituents of natural waters on the corrosion of copper pipes. In addition, Dr. Najm conducted numerous corrosion desktop studies for various public utilities evaluating various treatment technologies for reducing lead and copper corrosion in in-house plumbing. These utilities included the City of Fountain valley, the Las Virgenes Municipal Water District, and the Elsinore Valley Municipal Water District.

Water Treatment Process Testing & Evaluation

Dr. Najm was also project engineer on a biofiltration pilot plant project in Palm Beach, Florida. The pilot study aimed at investigating the use of ozone for the removal of color from Florida groundwater, as well as the use of biological filtration for the production of biologically stable water. The project included bench-scale testing of raw and finished waters for various water treatment parameters. Dr. Najm oversaw the operation and sampling of the pilot plant and the bench-scale experiments. The project also included monitoring of the distribution system for various water quality parameters, as well as biological growth. Hydrant flushing tests were conducted to determine the decay rate of chlorine in the distribution system. The project included mathematical modeling of the distributions system to estimate hydraulic residence times, and determine the effect of the existing hydrant flushing program on the hydraulic residence time in the distribution system, and thus the chlorine residual profile.

He was the project engineer on an American Water Works Association (AWWA) project that aimed at investigating the effect of coagulation and ozonation on the formation of disinfection by-products (DBPs). Eighteen utilities from across the United States participated in this.study. The project was supervised by the D/DBP Technical Advisory Workgroup (TAW). Dr. Najm served as the project manager of another AWWA project aimed at developing mathematical models for the prediction of trihalomethanes and haloacetic acids formation upon chlorination of natural waters.

Dr. Najm served as the project engineer on a bench- and pilot-scale evaluation of water treatment processes for the Long Beach Water Department, Long Beach, California. The objectives of the

study were to compare the applicability of direct filtration or conventional treatment to that of ozonation and biofiltration for the treatment of highly colored, arsenic-containing groundwater. The testing evaluated the removal of arsenic with enhanced coagulation on the bench-scale and the pilot-scale levels. Arsenic was spiked into the water to simulate worst case scenarios.

Dr. Najm was the project engineer on a bench-scale study for the Southern Nevada Water Authority. The objective of the study was to evaluate the removal of arsenic from surface water using enhanced coagulation with ferric chloride, and the removal of organic matter with enhanced coagulation and PAC adsorption.

Dr. Najm worked with the Elsinore Valley Municipal Water District on the performance optimization of a 9-MGD water treatment plant for the removal of natural organic matter. The treatment plant included an upflow floc-blanket reactor and dual media filters. Enhanced coagulation with alum, coupled with the addition of Powdered Activated Carbon (PAC) is used for the removal of taste-and-odor causing compounds and natural organic matter. The project also included a full review of the District's regulatory monitoring programs, development of deficiencies lists, and the development and implementation of revised monitoring programs to achieve regulatory compliance.

AWARDS: Dr. Najm is the recipient of the American Water Works Association's 1991 Academic Achievement Award for best doctoral dissertation.

ORGANIZATIONS: American Water Works Association
International Association on Water Quality
American Society of Civil Engineers
Sigma-Xi Research Society

PUBLICATIONS:

1. Trussell, R.R., I.N. Najm, "Feasibility of DBP Precursor Destruction With Advanced Oxidation Processes," In Preparantion.

2. Najm, I.N., W.H. Glaze, J.J. Lamb, R.P. Jackson, "A Demonstration of the Treatment of Munitions Residues in Groundwater by the PEROXONE Process," In Preparation.

3. Kawamura, S., I.N. Najm, K.M. Gramith, "Filter Trough Modifications to Minimize Media Loss During Filter Washing," *JAWWA*, **89**:12 (1997).

4. Najm, I.N., "Advances in the Mathematical Modeling of Powdered Activated Carbon Processes," *JAWWA* **88**:10 (1996).

5. Najm, I.N., and S.W. Krasner, "Effects of Bromide and Natural Organic Matter on the Formation of Ozonation By-Products," *JAWWA*, **87**:1 (1995).

6. Najm, I.N., N.L.Patania, J.G. Jacangelo, S.W. Krasner, "Evaluating Surrogates for Disinfection By-Products," *JAWWA*, **86**:6 (1994).

7. Najm, I.N., V.L. Snoeyink, Y. Richard, "Removal of 2,4,6-Trichlorophenol and Natural Organic Matter From Water Supplies Using PAC in Floc-Blanket Reactors," *Water Research*, **27**:4 (1992).

8. Najm, I.N., V.L. Snoeyink, T.L. Galvin, and Y. Richard, "Evaluation of Powdered Activated Carbon Use for the Control of Organic Compounds During Drinking Water Treatment," Final Report, AWWARF, (January 1991).

9. Najm, I.N., V.L. Snoeyink, and Y. Richard, "Effect of Initial SOC Concentration on its Activated Carbon Adsorption Capacity in Natural Water," *JAWWA*, **83**:8 (1991).

10. Najm, I.N., V.L. Snoeyink, B.W. Lykins, and J.Q. Adams, "Powdered Activated Carbon for Drinking Water Treatment: A Critical Review," *JAWWA*, **83**:1 (1991).

11. Najm, I.N. "Evaluation of the Use of Powdered Activated Carbon for the Control of Organic Compounds During Drinking Water Treatment," Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, Illinois (1990).

12. Najm, I.N., V.L. Snoeyink, M.T. Suidan, C.H. Lee, and Y. Richard, "Effect of Particle Size and Background Organics on the Adsorption Efficiency of PAC," *JAWWA* **82**:1:65-72 (1990).

13. Wang, Y.T., M.T Suidan , J.T. Pfeffer, and I.N. Najm, "The Effect of Concentration of Phenols on Their Batch Methanogenesis," *Biotechnology and Bioengineering* **33**:1353-1357 (1989).

14. Suidan, M.T., I.N. Najm, Y.T. Wang, and J.T. Pfeffer, "Anaerobic Biodegradation of Phenol: Inhibition Kinetics and System Stability," *Journal of Environmental Engineering, ASCE* **114**:6 (1988).

15. Najm, I.N., "Kinetics of Anaerobic Biodegradation of Phenolic Compounds," M.S. Thesis, University of Illinois at Urbana-Champaign, Urbana, Illinois (1987).

CONFERENCE PRESENTATIONS:

1. Najm, I.N., R.R. Trussell, E.M. Aieta. "Comparing Kinetic Models for *Giardia* and *Cryptosporidium* Inactivation With Ozone," Paper presented at the AWWA Water Quality Technology Conference, Denver, CO (November, 1997).

2. Najm, I.N., E.M. Aieta, J.A. Oppenheimer, B.T. Gallagher. "Impact of Natural Water Quality on the Inactivation of *Giardia* With Ozone," Paper presented at IWSA Conference, Madrid, Spain (September, 1997).

3. Trussell, R.R., I.N. Najm, "Feasibility of DBP Destruction With Advanced Oxidation Processes," Paper presented at the Disinfection By-Products Symposium, University of Houston, Houston, TX, March 20-21 (1997).

4. Najm, I.N., S. Liang, M. Davis, and E.M. Aieta, "Comparison Between RSSCT and Pilot-Scale GAC Performance for TOC Removal," Paper presented at the AWWA specialty

workshop on "GAC and Membranes: Bench- and Pilot-Scale Evaluations" in Cincinnati, OH (March 1996).

5. Najm, I.N., and J.P. Marcinko, "Impact of Analytical Methodology and Water Quality on TOC Analytical Results," In Proc. of the American Water Works Association Water Quality Technology Conference in New Orleans, LA (Nov. 1995).

6. Reich, K., I.N. Najm, K. Helm, and E.M. Aieta, "Industrial Use of Reclaimed Water: Implications of Water Quality", In Proc. of the Water Environment Federation Annual Conference in Miami Beach, FL (Oct. 1995).

7. Najm, I.N., S. Espinoza, J. P. Marcinko, C. H. Tate, and D. Selby, "Improving Enhanced Coagulation Performance With PAC Addition," In Proc. of the 1995 American Water Works Association Annual Conference, Anaheim, California (June, 1995).

8. Najm, I.N., "Advances in Mathematical Modeling of Powdered Activated Carbon Processes," Paper presented at the IWSA specialized conference on Activated Carbon in Drinking Water Treatment in Amsterdam, The Netherlands (September 1994).

9. Najm, I.N., and S.W. Krasner, "Effects of Bromide and Natural Organic Matter on the Formation of Ozonation By-Products," Paper presented at the 1994 American Water Works Association Annual Conference, New York City, New York (June 1994).

10. Najm, I.N. "Powdered Activated Carbon in Drinking Water Treatment," Paper presented at the 1994 American Water Works Association Annual Conference, New York City, New York (June 1994).

11. Najm, I.N., N.L. Patania, J.G. Jacangelo, and S.W. Krasner, "Effect of Coagulation on the Removal of DBP Precursors," Paper presented at the 1991 American Water Works Association Water Quality Technology Conference, Orlando, FL (November 1991).

12. Najm, I.N., and J.G. Jacangelo, "Formation and Control of Disinfection By-products," Paper presented at the 1991 annual conference of the California/Nevada section of the American Water Works Association, Anaheim, CA (October 1991).

13. Najm, I.N., V.L. Snoeyink, and Y. Richard, "Prediction Activated Carbon Capacities for Synthetic Organic Chemicals Present in Natural Waters," Paper presented at the 1991 American Water Works Association Annual Conference, Philadelphia, PA (June 1991).

14. Najm, I.N., V.L. Snoeyink, M.T. Suidan, and Y. Richard, "Powdered Activated Carbon in Floc-Blanket Reactors," presented at the 1989 American Water Works Association Annual Conference, Los Angeles, CA (June 1989).

BIOGRAPHICAL SKETCH

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Education:	PhD student, Northwestern University, 1997 to present. Master of Science in Civil Engineering (Environmental), Wayne State University, 1992; Civil Engineering, University of Buenos Aires, 1990
Professional Experience:	Harza Environmental Services, Hazardous/Industrial Waste Processing Section, Environmental Engineer, 1995 to 1997; Water/Wastewater Planning Section, Environmental Engineer, 1992-94. Ayres, Lewis, Norris & May, Inc., Ann Arbor, MI, Environmental Engineer 1990-92.
Professional Societies:	American Water Works Association, American Society of Civil Engineers, Water Environment Federation.
Professional Registrations:	Registered Professional Engineer in Wisconsin
Technical Papers:	"Using Chicago's Distribution/Tunnel Model for Practical Regional Decisions", AWWA Computer Conference (1996); "The Environmental Audit - First Step Towards Strategic Environmental Management," Power-Gen International Conference (1996); "Spreadsheet Models for Groundwater Flow and Contaminant Transport", AWRA Symposium on Water Resources Education, Training, and Practice (1997).

SELECTED PROJECTS:

Iowa Army Ammunition Plant Groundwater Investigation
Client: Us Army Corps Of Engineers Omaha District
Site Manager for groundwater investigation. Responsible for seven-man team of professionals and three teams of drillers performing installation and sampling of groundwater wells, hydropunch wells, soil borings, piezometers, minipiezometers, monitoring well inspection and survey, hydrological modeling and flow measurements, bedrock exposure survey, and well slug-tests. (1997)

SIDOR Environmental Audit, Venezuela
Client: C.V.G. Siderurgica del Orinoco (SIDOR)

Project consisted of comprehensive multimedia environmental audit for 3 million ton per year iron and steel mill, including evaluation of existing waste control systems, determination of compliance/non-compliance of discharges, and development of conceptual corrective actions to bring facilities into regulatory compliance. As overall Project Engineer and Lead Engineer for solid and hazardous wastes, sanitary wastewater, and storm water: inspected all solid waste, hazardous waste, sanitary wastewater and storm water management facilities; arranged and supervised preliminary site remedial investigation including sampling of surface and subsurface soils, sediments, and groundwater; reviewed historical discharge records for wastewater and storm water to determine compliance with applicable U.S. and Venezuelan environmental

regulations; compared soil, sediment, and groundwater to RBCs; developed conceptual corrective actions for soil and groundwater; developed conceptual corrective actions for wastewater and storm water management systems; coordinated activities by Harza staff, one U.S. subconsultant and two Venezuelan subconsultants for auditing and development of corrective measures for air emissions and industrial wastewater; and prepared interim technical memoranda and final report (1995-96).

Bedford Park Water System Assessment, Bedford Park, Illinois
Client: Bedford Park

As Staff Engineer for water system study for the Village of Bedford Park, IL, developed demand projections throughout year 2025, prepared CYBERNET distribution system model, calibrated model by field testing, and used model to determine required improvements to serve future demands. The purpose of the study was to identify current and future improvements to piping, pumping, and storage facilities in Bedford Park required to facilitate conveyance of water supply from receiving points from the City of Chicago to delivery points to a potential purchaser for wholesale supply to other communities in southwest suburban Chicago. Projected 2025 peak supply was estimated at as much as 112 MGD (4.9 m^3/s), up from the current 20 MGD (0.9 m^3/s) peak supply (1995).

Pollution Prevention Feasibility Study for Jordan Petroleum Refinery Company (JPRC), Jordan
Client: USAID

As Project Engineer, evaluated the technical, economic and environmental feasibility of conceptual options for treating and recycling of process wastewater. The option determined to be the most feasible was to upgrade the existing wastewater treatment system (air flotation and biological treatment) with filtration and carbon adsorption and reuse wastewater as cooling tower makeup water. The addition of reverse osmosis to the cooling towers would further increase water savings. The implementation of this project would reduce wastewater discharge, conserve water, and would provide a payback period of 8 years. The selected option was subsequently implemented in pilot scale as a demonstration project (1995).

Chicago Comprehensive Study for Adequate Water Supply, Chicago
Client: Chicago Department of Water

Project Engineer for comprehensive water supply master plan for City of Chicago water system. Project included identification of required improvements to water treatment and distribution facilities in order to satisfy future demands through year 2030, and a feasibility study of conversion of existing steam pump stations to electric prime movers. In 1992 the system supplied an average day flow of 1,200 mgd to approximately 5 million people. Developed population and demand projections; developed peaking factors for City and suburban customers; implemented enhancements to the existing 1,000-pipe WaterMax distribution system model including the addition of pump curves, a high pressure service main, and the revision of average day demands, peaking factors, and C-factors for current and future conditions; calibrated model by using field data from peak demand events; developed and calibrated tunnel model; and used distribution and tunnel system models to develop phased capital improvements program through year 2030, amounting to over $40 million. Used the tunnel and distribution models to investigate conceptual supply alternatives, scenarios of construction timing, and peak/off peak demand management. Other responsibilities during the project included preparation of interim technical memoranda, reports, and coordination of work by three subconsultants (1994-95).

Lake of Guadalupe Feasibility Study, Mexico
Client: Secretariat of Ecology, State of Mexico

Lead Engineer for feasibility study to reclaim Lake of Guadalupe, a hypereutrophic lake in the metropolitan area of Mexico City impacted by untreated wastewater discharges from a tributary population of over 200,000 within a 250-ha basin. Tasks performed included: land use analyses; population projections; assessments of existing wastewater collection systems; sampling and analysis of tributaries, lake water, and lake sediment; development and calibration of a lake water quality model; and development of a comprehensive regional water resource management plan including water and wastewater facilities, a phased implementation plan, and a project financing package (1993).