



Carbon Augmentation for Biological Nitrogen Removal



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The 2008 *Carbon Augmentation for Biological Nitrogen Removal Compendium* was written to identify knowledge gaps to be addressed by the Nutrient Removal Challenge. That document contains state-of-the-art knowledge to achieve reliable, cost-effective nutrient removal. The 2008 compendium included a number of questions and challenges to reduce nutrients in advanced treated wastewater. This 2019 compendium revision contains a summary of the findings generated by the researchers and contributors.

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●●●● BACKGROUND AND DEFINITIONS

Why is Carbon Augmentation Required to Accomplish Greater Levels of Nitrogen Removal?

Biological nitrogen removal involves a two-step aerobic/anoxic process of nitrification and denitrification. First, the ammonia-nitrogen in the wastewater is biologically oxidized to nitrite and nitrate by autotrophic organisms under aerobic conditions. Then, these compounds are reduced to nitrogen gas in anoxic zones (denitrification) by heterotrophic organisms in the absence of dissolved oxygen. In the denitrification step, carbon is used as an electron donor by denitrifying bacteria with nitrate and nitrite reduction for energy production and new biomass growth.

Carbon sources could be from the influent wastewater, the substrate released by endogenous decay of biomass, or an external source. The rate of denitrification is dependent on three things: the denitrifying biomass concentration, the concentration of nitrate/nitrite, and the biodegradable soluble organic carbon concentration. Carbon augmentation is used when there is insufficient carbon available to achieve the level of nitrate removal desired in the time available. External carbon is more often needed if complete denitrification is needed to meet low levels of effluent total nitrogen (e.g., < 5 mg/L TN). It may also be needed for nitrogen removal with influent wastewaters having BOD:N ratios < 4.0.

What Biological Nitrogen Removal Processes Typically Require Carbon Augmentation?

External carbon can be added to the pre-anoxic and/or post-anoxic zones in several activated sludge configurations designed for biological nitrogen removal. Carbon augmentation is required in tertiary denitrification applications, such as denitrification filters, moving bed biofilm reactors (MBBRs), and biological aerated filters (BAFs). Examples of common process configurations of denitrification using external carbon sources can be found in the latest edition of WEF/ASCE *Design of Municipal Wastewater Treatment Plants*, WEF Manual of Practice No. 8.

What Are Typical Effluent Inorganic Nitrogen Concentration Goals for Systems with Carbon Addition?

Dissolved organic nitrogen concentrations in the clarified effluent of a biological nitrogen removal process could be in the 1-2 mg/L TN range, depending on a variety of factors such as influent wastewater characteristics, process configuration, and operational practices. This means that for applications in which very low effluent nitrogen levels are required (e.g., < 3 mg/L TN), the allowable concentration of inorganic nitrogen must be less than 1 to 2 mg/L TN. To meet these requirements, essentially complete nitrification and denitrification is required. Very low levels of ammonia-nitrogen (< 0.5 mg/L TN) can be reliably accomplished by a well-designed and operated nitrifying activated sludge process. Therefore, the denitrification process needs to consistently achieve $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$ ($\text{NO}_x\text{-N}$) concentration in the 0.5 to 1.5 mg/L range. Achieving these very low levels requires carbon augmentation.

What Are Typical Hydraulic and Solid Retention Times Used for Post-anoxic Zones with Carbon Augmentation?

There are a number of activated sludge configurations that include a post-anoxic zone to achieve higher levels of denitrification. Typical hydraulic detention times are two to four hours hydraulic retention time (HRT) (WEF 1998). Recent studies (Mokhayeri et al. 2006) associated with high denitrification requirements at low temperature applications indicate that anoxic basin solids retention times (SRTs) should be in excess of one day to provide sufficient levels of highly specialized methanol-utilizing organisms.

The post-anoxic zone HRT depends on the amount of oxidized nitrogen removal needed and the rate of denitrification for a given external carbon dose. At higher carbon dose rates, the reactor carbon concentration will be increased, which increases the denitrification rate and reduces the anoxic reactor HRT. However, a larger portion of the carbon added leaves in the anoxic reactor effluent flow and is not used for NO_x reduction to thus increase the carbon dose.

What Are Key Process and Design Issues Related to Carbon Augmentation?

- **Carbon Type**

Different carbon substrates have different biomass synthesis yield coefficients (g VSS produced/g COD used), which then affects the portion of the substrate used for NO₃-N reduction. Substrates, such as glycerol versus methanol, have a higher synthesis yield, which results in higher carbon dose due to the use of a smaller fraction of the substrate added for NO₃-N reduction. The same applies for NO₂-N reduction.

- **Minimization of DO Addition to the Anoxic Zone** (where carbon would be consumed for oxygen utilization before NO_x reduction)

Denitrifying bacteria use oxygen faster than they use NO₃-N and NO₂-N.

- **Carbon Dose, kg Carbon/kg NO₃-N Removed**

The carbon dose is affected by the substrate type, amount of oxygen entering the anoxic zone, and the anoxic zone substrate concentration. Higher anoxic zone substrate concentrations drive a faster denitrification rate but result in more of the carbon added in the anoxic zone effluent.

- **Anoxic Zone Detention Time**

The anoxic zone detention time is affected by the amount of NO₃-N to be removed, denitrifying biomass concentration, temperature, carbon type, and anoxic zone augmented carbon concentration.

- **Ability of Biomass to Readily Use Carbon Source in Response to Variable Influent NO_x Concentrations and Temperature and pH Changes**

A faster response to changing NO_x-N concentrations and reactor conditions occurs when using carbon sources (i.e., acetate) that can be degraded by heterotrophic biomass growing

on other influent wastewater substrates. Methanol fed systems are less responsive due to the need to develop the specialized methanol-degrading bacteria population.

- **Control of Carbon Dose to Minimize Amount in Effluent**

Influent nitrogen loadings can vary by a factor of 1.5 to 2.0 from typical diurnal loadings alone to result in variable NO_x-N loadings to the anoxic zones. Online control systems are more effective for changing the carbon dose with changes in influent loadings and operations than by manual operation.

- **Carbon Handling and Storage Facilities**

The carbon type affects the handling and safety issues and thus the design of the carbon storage and feeding facilities.

Why Is Methanol the Most Commonly Used External Source for Carbon Augmentation?

Methanol is the most commonly used and best documented carbon augmentation source for biological nitrogen removal. It has traditionally been the least expensive source (in terms of chemical cost per mass of N removed) as compared to other known carbon sources, such as acetic acid and ethanol. Methanol has a relatively low biomass yield, which is an important consideration as it impacts the methanol dose and residual sludge handling and disposal. It is important to recognize the relationship between the biomass yield for a given substrate and the ratio of kg COD required/kg NO₃-N removed.

A common term developed by McCarty et al. (1969) to relate carbon dose to the type of substrate is the consumptive ratio. They showed that the consumptive ratio is a function of the biomass synthesis yield for a given substrate as shown by equations 1 and 2 below.

Equation 1: Nitrate Reduction

$$C_{R,NO_3} = \frac{\text{g COD}_{\text{consumed}}}{\text{g NO}_3\text{-N}_{\text{removed}}} = \frac{2.86}{1-1.42Y}$$

C_{R,NO_3} = Consumptive Ratio for Biological Nitrate Reduction, g COD/g NO₃-N

Y = g VSS Produced/g COD Used

Equation 2: Nitrite Reduction

$$C_{R,NO_2} = \frac{\text{g COD}_{\text{consumed}}}{\text{g NO}_2\text{-N}_{\text{removed}}} = \frac{1.72}{1-1.42Y}$$

C_{R,NO_2} = Consumptive Ratio for Biological Nitrite Reduction, g COD/g NO₂-N

As the anoxic biomass yield for a given substrate decreases, a larger fraction of the substrate added will be oxidized to generate energy, at the expense of the electron acceptor. In this case

the amount of substrate added per unit of NO_x removed is less. Because methanol has a low yield under anoxic degradation (in the range of 0.25 to 0.40 g biomass VSS/g COD) a larger fraction of the methanol added is used for nitrate/nitrite reduction.

Methanol has the lowest required consumptive ratio or lowest dose compared to other supplemental carbon sources used. Its cost is also competitive with other supplemental carbon sources so that it has the lowest cost per unit of NO_x removed. This comparison assumes that little methanol remains in the anoxic zone effluent.

While the lower biomass yield and cost are favorable factors for the use of methanol, two important disadvantages are its lower nitrate reduction kinetics and the inability of common heterotrophs in municipal activated sludge processes to use methanol. The lower nitrate reduction kinetics have a greater impact at lower temperature, and if the anoxic volume is limited, an elevated methanol concentration in the anoxic reactor effluent occurs to maintain the necessary denitrification rate, which then results in a higher methanol dose. The need to have an acclimated methanol-degrading population means that methanol addition needs to be maintained at some level to provide an active population to handle intermittent carbon augmentation needs or to provide a startup population for seasonal nitrogen removal.

What Is Driving the Current Interest in Carbon Augmentation Alternatives to Methanol?

The interest in other supplemental carbon sources is a result of three disadvantages for using methanol: (1) an acclimated microbial population grown on the methanol added is required, (2) the methanol-degrading culture has much lower denitrification kinetics, and (3) methanol poses special safety issues. Common activated sludge microorganisms cannot use methanol, and thus an acclimated culture grown from the methanol added must be developed and maintained. This is a clear disadvantage for cases where supplemental carbon is needed on an intermittent basis or for highly variable supplemental carbon needs due to varying NO_x concentration. The lower denitrification kinetics for methanol requires a much larger postanoxic reactor compared to other carbon sources. Special design precautions are needed to provide adequate operations and storage safety due to the high flammability of methanol.

The above issues coupled with an expanding non-wastewater market for methanol and price uncertainty has motivated our industry to more often consider alternative carbon augmentation sources. Glycerol, ethanol, and acetate have been considered.

●●●● FUNDAMENTAL PROCESS AND DESIGN ISSUES

What Determines External Carbon Dose?

Using Equation 1 the COD consumed to NO₃-N removal ratio for methanol is 5.0 g COD/gNO₃-N, assuming a synthesis yield of 0.30 g VSS/g COD used. The dose based on methanol concentration is 3.3 g methanol/g NO₃-N used as 1 g methanol is equivalent to 1.5 g COD. A commonly expected dose for methanol use in post anoxic denitrification filters is in the range of 3.3 to 3.5 mg/L methanol per mg/L of NO₃-N removed. However, in activated sludge post anoxic applications to meet low effluent NO_x concentrations much higher doses have been required.

The reasons behind the higher doses used may be related to number of efficiency issues, such as:

- Incomplete Mixing
- Excess DO Entering the Anoxic Zone
- Methanol Feed Control Strategy
- Nitrate Measurement Accuracy
- Unused Methanol in the Post-anoxic Reactor Effluent Flow
- Reactor Design

If methanol is added to the post-anoxic zone, the following equation can be used, assuming a methanol synthesis growth yield of 0.30 g VSS/g COD, complete methanol consumption, and no substrate provided by mixed liquor endogenous decay, to estimate the required dosage rate (customary units) (WEF MOP 29):

Equation 3:

$$\text{Methanol Dose Rate (lb/d)} = (Q_{in} + Q_{ras})(NO_3-N_{in} - NO_3-N_{out})(3 \text{ mg MeOH/mg } NO_3-N_{removed})(8.34)$$

where:

Q_{in} = Biological Reactor Influent Flow, mgd

Q_{ras} = Return Activated Sludge Flow, mgd

NO_3-N_{in} = Nitrate Entering Post-anoxic Zone, mg/L

NO_3-N_{out} = Target Effluent Nitrate from Post-anoxic Zone, mg/L

What Key Fundamental Kinetic Parameters Are Needed to Define the Rates and Efficiency of Using an External Carbon Source?

Stoichiometric and kinetic parameters are used to model nitrogen removal systems. The key fundamental kinetic parameters and their effects on design are listed in Table 1.

Table 1 - Kinetic Parameters and Their Effects

Parameter	Definition	Effect
Y	Synthesis Yield, g VSS/g COD	Lower yields result in less carbon (on a COD basis) needed per g of NO ₃ -N removed
b	Endogenous Decay Coefficient, g VSS/g VSS-Day	Lower b in overall system requires more substrate to maintain active organisms
μ_m	Maximum Specific Growth Rate, g VSS/g VSS-day	Lower values require larger tanks and longer SRTs for efficient substrate utilization
K _s	Carbon Source Half Velocity Coefficient, mg/L COD	Lower values require less substrate use and less residual carbon in the effluent

What Is the Effect of Temperature on External Carbon Dose and Post-anoxic Tank Design?

Post-anoxic zone capacity requirements substantially depend on the growth rate of substrate-specific heterotrophic bacteria and corresponding active fraction of these organisms in the mixed liquor. Results from the study conducted at Blue Plains AWTP suggest that the maximum specific growth rate (μ_{max}) for methanol utilizers at 19°C is double the μ_{max} obtained at 13°C and denitrification with methanol addition does not achieve low total nitrogen values during the winter (Mokhayeri et al. 2006). This implies that either considerable post-anoxic zone volume would be required for cold temperature operation and/or that alternative carbon augmentation sources with more favorable kinetic characteristics (such as glycerol, ethanol, or acetate) be employed in winter months.

●●●● CARBON AUGMENTATION WITH METHANOL

What Bacteria Consume Methanol for NO_x Reduction and What Are Their Characteristics?

When using methanol to supplement denitrification at a WWTP it is important to consider the microorganisms present in a methylophilic denitrifying biomass, and the sensitivity that might be associated with them. Aerobic high-rate BOD removal and heterotrophic denitrification using influent BOD or a wide range of other external carbon sources in a WWTP can be performed by a very large array of microorganisms, but this is not the case for some nutrient removal processes. Biological denitrifying methanol-utilizing bacteria are a very specific group of microorganisms, and thus makes the treatment process more susceptible (Heylen et al. 2005).

Due to the initial low concentration of methylotrophs in activated sludge, a lag period is observed when first adding methanol for denitrification. This acclimation period, likely associated with the growth and establishment of a new population of methylotrophic organisms can last between a few days to many weeks depending on the situation and conditions (e.g., temperature) in the reactor (Carrera et al. 2003). Therefore, methanol dosing may be required consistently to maintain the specific biomass after acclimation. This population shift has been visualized with molecular tools in other papers such as Hallin et al (2006) and Ginige et al (2003).

The environmental conditions present in a WWTP tend to select for specific microorganisms. Methylotrophic bacteria can be divided into three subgroups: the obligate methylotrophs that can use only single-carbon compounds; the restricted facultative methylotrophs that also grow on a limited range of more complex organic compounds (ethanol, propanol); and typical facultative methylotrophs that grow on a wider range of polycarbon compounds (acetate, glucose) (Doronina et al. 2005).

Microorganisms that have been reported to be responsible for denitrification in activated sludge are varied. This could be due to the limitations of bacterial culture techniques from biological treatment process samples, the molecular methods used for identification, or simple differences in reactor conditions. Magnusson et al (1998) reported that all of the denitrifying methanol-utilizing strains were Gram negative proteobacteria, facultative aerobic motile rods. Multiple culture-dependent techniques have suggested that *Hyphomicrobium* spp. and/or *Parococcus* spp. were the dominant species associated with methanol-driven denitrification; and therefore, the likely methylotroph present in post-denitrification processes (Timmermans and Haute 1983, Neef et al. 1996, Foglar and Briski 2003, Lee and Welander 1996, Lemmer et al. 1997). The weakness of using culture-based methods is that they can fail to accurately represent the microbial community structure since function cannot be directly linked to identity (Wagner et al. 1993). Using methods such as stable-isotope probing (SIP) can help to overcome some of these limitations. SIP uses ¹³C substrates to biologically label the DNA of microorganisms responsible for using that substrate (Radajewski et al. 2000).

The use of SIP has suggested that methylotrophs that were not previously known as denitrifiers in activated sludge could be selected in the process. Ginige et al (2004) and Osaka et al (2006) have suggested microorganisms closely related to obligate methylotrophs *Methylobacillus* and *Methylophilus* in the order of methylophilales of beta-proteobacteria are responsible for denitrification with methanol. Ginige et al (2004) also reported that there was no correlation between denitrification rates and *Hyphomicrobium* abundance.

Chandran and Sandino (2012) used SIP to determine the population of methylotrophs grown with methanol as the electron donor and nitrate as the electron acceptor in an activated sludge mixed liquor. Most of the ¹³C-carbon as methanol was incorporated into methylotrophic bacteria mass, with a little leaking out to other organisms due to endogenous decay. Centrifugation separated the heavy DNA from the lighter DNA and sequencing of the separate heavy DNA, which was sequence to identify the bacteria responsible for denitrification using methanol.

Two types of bacteria were found: *Hyphomicrobium* spp. and *Methyloversatilis* spp. *Hyphomicrobium* is known to be capable of nitrate reduction with methanol, but the presence of *Methyloversatilis universalis* in this type of system was a new finding. In addition, the investigators also found that *Methyloversatilis* could use ethanol, while *Hyphomicrobium* could not as expected. Further studies by Lu et al. (2012) found that the *Methyloversatilis* could only reduce nitrate to nitrite. The ability of the *Methyloversatilis* to switch between methanol and ethanol is important for systems in which the choice of supplemental carbon might change with changes in temperature.

SIP was also used to assess populations capable of glycerol degradation under denitrification. These were a more diverse population including *Comamonas* spp. and *Diaphorobacter* spp. in suspended growth, and *Comamonas* spp., *Bradyrhizobium* spp., and *Tessaracoccus* spp. on fixed film media. They also found that the denitrification kinetics using glycerol were about three times faster than that for growth with methanol.

The results of these studies show the important of relating biological kinetics for a given system with knowledge of the microorganism that dominate.

What Are the Key Stoichiometric and Kinetic Coefficient Values for Methanol under Anoxic Conditions?

A summary of kinetic coefficient values reported in the literature from several sources are shown in Table 2.

Table 2 - Stoichiometric and Kinetic Coefficients Methanol Denitrification

COD/N	Y (gVSS/gCOD)	μ_{max} (d ⁻¹)	b (mgN/gVSS-h)	Reference
			2.3	Monteith et al. 1980
			3	Nyberg et al. 1996
			8.7-13.3	Beccari et al. 1983
4.6			4.28	Bilanovic et al. 1999
			5-6	Bailey et al. 1998
		0.52 (10°C) - 1.86 (20°C)		Stensel et al. 1973
4.7		0.4-0.5 (13°C) - 1.0 (19°C)		Mokhayeri et al. 2006
		0.56 (13°C) - 6.29 (20°C)		Dold et al. 2005
4.1 - 4.5	0.23 - 0.25	0.77 (15°C) - 2 (20°C)	32 (15°C) 91 (20°C)	Christensson et al. 1994 Pure Culture
3.57		0.67 - 1 (15°C)	29	Lee and Welander 1996
	0.5 - 0.65			Henze et al. 1995
	0.18	0.52 (10°C) - 1.86 (20°C)		Tchobanoglous et al. 2003
			2.4-3.6	Fillos et al. 2007
3.7			1.7 (10°C) - 6.72 (25°C)	Carrera et al. 2003
			9.6	Peng et al. 2007

Source: Adapted from Gu and Onnis-Hayden 2010

What Is the Range of Typically Expected Methanol Doses for NO_x Removal in Lb Methanol/Lb NO₃-N Removal When Most of the Methanol Added Can Be Used in the Post-anoxic Tank?

Typically methanol dosages are reported as 3.0 – 3.3 mg methanol per mg nitrate denitrified; that is, 4.7 – 5.0 mg COD / mg NO₃-N. For a true anoxic yield for methylotrophic organisms of 0.28 g VSS/g COD, the expected carbon usage ratio is 4.8 g COD/g NO₃-N or 3.2 g MeOH/g NO₃-N.

What Happens to the Methanol Used in an Aerobic Tank After the Post-anoxic Tank and Its Effect on Overall Denitrification Rates in the Post-anoxic Tank?

There is considerable uncertainty associated with the denitrification potential of aerobically grown methylotrophic bacteria and its effect on full-scale plant design/operation. Some research suggests that methylotrophs grown under aerobic conditions could have lower growth rates (and lower nitrate reduction rates) under anoxic conditions (Table 3). Thus, system with excess methanol feeding and removal in downstream aerobic zones may result in less efficient denitrification rates relative to the amount of methanol fed and perhaps different methylotrophic populations.

Table 3 - Reported Methylo-trophic Kinetics at 20°C

Growth Condition	μ_{\max} , Aerobic	μ_{\max} , Anoxic	Temp. θ	Source
Anoxic	1.72	1.30		Purtschert/Gujer 1999
Aerobic	3.88	0.81		Purtschert/Gujer 1999
Anoxic		1.86	1.12	Stensel 1973
Anoxic		1.13	1.13	Nichols et al. 2007
Anoxic		1.30	1.072	BioWin Model Default

Source: Dold et al. 2008

On the other hand, preliminary results from a study conducted at the Blue Plains AWTP aimed at evaluating methods for possibly overcoming limitations of methanol addition for full-scale facilities that have limited available cold-weather anoxic solids retention time (SRT) (Parsons et al. 2007), indicate that aerobically grown methylo-trophs have the potential to denitrify with kinetics similar to that grown anoxically and that a bleed of methanol into the aerobic zone of a BNR process could alleviate anoxic capacity limitations, albeit with increased methanol demand.

What Is the Typical Design Approach for Maximizing Methanol Use Efficiency in Carbon Augmentation?

The design of a methanol dosing system (anoxic tank volume, methanol dose, sludge production, and start-up strategy) requires detailed knowledge of the stoichiometry and kinetics of the growth and decay processes of methylo-trophs under anoxic and aerobic conditions. The size of the anoxic reactor is related to the denitrifying population concentration, the methanol feed rate, and the methanol utilization kinetics. Nitrate consumption is estimated in a similar manner as supplying oxygen for an aerobic process. The most efficient design is a staged reactor system (duplicated in many cases by complete mix activated sludge (CMAS) units in series), in which the electron donor (carbon) is methanol, and the electron acceptor is $\text{NO}_3\text{-N}$. However, additional mixing equipment and baffles are needed. The reactor in series system increases the rate of denitrification because of the higher concentration of nitrate and methanol in the initial stages.

What Are the Advantages and Disadvantages of Using Methanol for Carbon Augmentation?

Advantages:

- Apparent Cost Advantage
- Ample Experience
- Easy to Apply
- Low Sludge Production

Disadvantages:

- Explosive Chemical (Burns without Visible Flame)
- Requires a Specialized Group of Organisms
- Lower Response Rate to Changing and Intermittent Carbon Needs
- Price Volatility
- Availability

●●●● OTHER CARBON AUGMENTATION SOURCES

Though the substrate unit costs may be higher for some alternative carbon sources compared to methanol, a significant advantage for the alternative carbon is allowing the use of a smaller anoxic tank. In addition, the alternative carbon source could be used on a seasonal basis, such as winter operation when higher kinetic rates than that for methanol are preferred.

What Are the Desirable Characteristics of a Carbon Augmentation Source?

The ideal carbon augmentation source for enhanced denitrification will have the following properties:

- Ability to produce a rapid denitrification rate (mass $\text{NO}_3\text{-N}$ /mass volatile suspended solids/day)
- Low substrate requirement for denitrification (mass chemical/mass $\text{NO}_3\text{-N}$) to minimize chemical costs
- Degradable by facultative heterotrophic bacteria commonly found in mixed liquor
- Low biomass yield to reduce solids processing impacts (directly proportional to low substrate requirement)
- Contain minimal nitrogen or phosphorus
- Contain no contaminants that will affect nitrification rates, sludge quality, or effluent quality
- High concentration to minimize storage requirements
- Low cost
- Reliable supply
- Avoid special storage and feed requirements (i.e. phase separation, suspended solids, freezing/gelling, high viscosity)

What Are Some Other Carbon Augmentation Sources?

External carbon sources that can potentially support denitrification can be categorized as: (1) pure chemicals like methanol, ethanol, acetate, sugar, butanol, etc.; (2) purified agricultural or industrial byproducts such as corn syrup wastes; (3) raw industrial/agricultural byproducts such as molasses, biodiesel glycerol waste, brewery waste, and other process wastes; (4) sludge fermentation products; and (5) others compounds, such as hydrogen, methane, H_2S and elemental S.

Relevant information on primary sludge fermentation can be found in the Nutrient Removal Challenge Compendium *Fermenters for Biological Phosphorus Removal Carbon Augmentation* (WRF 2019).

What Are Some of the Pure Chemical Alternatives to Methanol Also Used as External Carbon Sources?

Acetic acid, sodium acetate, and ethanol are the most common pure chemicals that have been considered as an alternative to methanol as external carbon sources for denitrification. Acetic acid has been used by several utilities, but its cost has been historically higher than methanol. Acetate has demonstrated higher removal rates than methanol (Gerber et al. 1986, Tam et al.

1994, Mokhayeri et al. 2008), likely as the result of sodium acetate being a directly utilizable substrate, and more readily metabolized by a much wider variety of heterotrophs than methanol. Sodium acetate, however, requires dry chemical handling and feeding systems.

Ethanol is also easier to metabolize than methanol and thus results in higher denitrification rates, especially at low temperatures at which methylotrophs slow down considerably. Recent studies conducted by NYCDEP (Tsuchihashi et al. 2007) have looked into the operational strategy of switching from methanol feed to ethanol for cold weather denitrification. The challenge with ethanol, however, lies also in its high cost, as it is commonly more expensive than methanol. There is also the concern of maintaining appropriate bacterial populations when switching back and forth. See Table 4 for a compilation of kinetic coefficients for denitrification with acetic acid, acetate, and ethanol (Gu and Onnis-Hayden 2010).

Table 4 - Denitrification Kinetic Coefficients Using Acetic Acid, Acetate, and Ethanol					
Carbon Source	COD/N	Y (gVSS/gCOD)	μ_{max} (d ⁻¹)	b (mgN/gVSS·h)	Reference
Ethanol		0.25-0.28	1.89 (15°C) - 4.8 (25°C)	46 (15°C) 139 (20°C)	Christensson et al. 1994 Pure Culture
				5.6	Fillos et al. 2007
				10	Nyberg et. al 1996
				12	Peng et al. 2007
			0.22		Hallin et al. 1996
Acetate				4-7	Naidoo et al. 1998
				2.08-3.53	Isaacs and Henze 1995
				10.4	Carucci et al. 1996
				7.95-10.6	Tam et al. 1992
				3.2	Karlsson 1990
				10-20	Henze et al. 1994
				9.89	Bilanovic et al. 1999
			0.32		Muller et al. 2003
				3.2	Peng et al. 2007
			0.66		Kujawa and Klapwijk 1999
	3.5		1.2 (13°C) 3.5 (19 °C)		Mokhayeri et al. 2006
Acetic Acid COD: 1121000 mg/l				27	Akunna et al. 1993
	4		2.18 (15°C)	49-76	Lee and Welander 1996
				2.2-2.5	Gerber et al. 1986

Source: Adapted from Gu and Onnis-Hayden 2010

What Fundamental Process Information Is Known about Commercial Proprietary Carbon Sources?

In recent years, there has been an interest in the development of commercial proprietary external carbon sources. One currently being marketed is MicroC™, a purified agricultural industry byproduct. This product is developed by Environmental Operating Solutions, Inc. and designed specifically for use as an electron donor/carbon source for biological denitrification of wastewater. MicroC™ was developed as a viable alternative carbon source to methanol without the safety hazards. Technical specifications and Material Safety Data Sheets can be found at www.microc.com/products/

What Are Some Waste Products Used for Carbon Augmentation?

Glycerol, a by-product of biodiesel production, and glycerol solutions such as unicarb-DNTM, which is made by Univar, have been recently proposed as external carbon for denitrification but relatively little data is available on its applications. Ramalingam et al. (2006), in a pilot study conducted in collaboration with the NYCDEP using biodiesel waste, found an average denitrification rate of 1.8 mgN/gVSS/h. They also highlighted the need for acclimatization of the biomass to efficiently removed the nitrate (Onnis-Hayden and Gu 2008).

●●●● OPERATIONAL CONSIDERATIONS

How Do You Control Carbon Augmentation Feed Rate?

Carbon augmentation feed control strategies include manual control, automatic flow-paced control, automatic feed-back control using flow and effluent nitrate concentration, automatic feed-forward control using flow and influent nitrate concentration, and automatic feed-forward and feedback control using flow, as well as influent and effluent nitrate concentrations. The last three modes, although increasingly complex, are considered essential when low TN levels are required. They rely heavily on online monitoring systems, and fortunately, there has been recent advances on this regard with newer instruments that are more durable and maintain their calibration for longer periods. Also, there are patented instrumentation packages available, aimed at providing very low effluent nitrate levels while maintaining low BOD and TOC levels as well. Examples of online nitrate analysis instruments include Hach Nitratax, Endress+Hauser Stamosens, and Applied Spectrometry Associates, Inc. ChemScan.

What Safety Issues Are Associated with the Use of Methanol as a Carbon Augmentation Source?

Methanol is a colorless volatile liquid with a faintly sweet, pungent odor similar to ethyl alcohol. The substance is fully soluble in water. Vapors of methanol are slightly heavier than air and may travel some distance to a source of ignition and flash back. Accumulations of vapors in confined spaces such as buildings or sewers may explode if ignited. Methanol is highly flammable, with a flash point of 12°C (54°F). There is potential for containers of liquid to rupture violently if exposed to fire or excessive heat for sufficient time duration. Methanol fires are also particularly problematic because it burns without a visible flame. Methanol is listed as a “Poison-Class B.” It is harmful if swallowed or absorbed through the skin. Ingestion of as little as one ounce can cause irreversible injury to the nervous system, blindness, or death. It cannot be made nonpoisonous. It causes eye and respiratory system irritation and may cause skin irritation. Liquid, mist, or vapor contact should be avoided. Vapor inhalation or liquid penetration of the skin can cause central nervous system depression.

Specific information regarding safe handling and storage recommendations, health effects, and appropriate methanol emergency response can be found in the *Methanol Safe Handling Manual* on the Methanol Institute website:

www.methanol.org/safe-handling/

A source of information on methanol storage tank design stems from the methanol tank explosion at the Bethune Point WWTP in January 2006, specifically the final report completed by the U.S. Chemical Safety and Hazard Investigation Board:

www.csb.gov/bethune-point-wastewater-plant-explosion

●●●● TESTING DIFFERENT CARBON SOURCES FOR A FACILITY

What Are Goals and Methods for Testing External Carbon at Bench Scale?

In general terms, testing of carbon sources are aimed at defining the rate and extent of their biodegradability, synthesis yield coefficient, and growth and substrate utilization kinetic parameters necessary to model the system at the anticipated operating conditions. A Nutrient Removal Challenge report by Gu and Onnis-Hayden (2010) provided a guidance document for a comprehensive and practice-orientated standardized methodology and a procedure to assess the efficiency and feasibility of an alternative carbon augmentation source for enhancing nitrogen removal at full-scale WRRFs. A road map is developed that depicts the overall framework and identifies the key components required for a comprehensive and systematic assessment of an alternative carbon source for denitrification. A prescreening procedure for carbon alternatives is established and an evaluation matrix is provided. The document presents a list of basic parameters that should be obtained or measured to assess the potential of a carbon source. These basic parameters can be used to determine the carbon dose and process performance monitoring.

What Can Be Learned by Full-scale Testing?

Conducting lab tests under controlled conditions allows for a comparative evaluation between carbon sources but is not as effective at predicting the actual performance of a full-scale system, as they don't take into account the reality of variable loading conditions, operating conditions, and operating temperatures.

●●●● RESEARCH NEEDS

What Are Some of the Research Needs to Improve Understanding, Process Efficiency, and Design Reliability of Carbon Augmentation for Nitrogen Removal?

- Investigate other waste products, such as fermenting food waste etc., to provide lower-cost carbon sources.
- Advance the ability of online instrumentation and control for optimal operation and performance of biological nitrogen removal systems.
- Investigate the use of other carbon sources with methanol addition to handle variable carbon needs under transient conditions and lower temperature operation.
- Determine the potential for using fixed film media in pre- or post-anoxic zones to reduce the anoxic zone detention time and improve carbon utilization efficiency.
- Investigate the use of carbon augmentation in emerging granular sludge activated systems for nutrient removal.

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