

GOT CARBON?

Widespread biological nutrient removal is increasing the demand for supplemental sources

Christine deBarbadillo, James Barnard, Steve Tarallo, and Mark Steichen

As more wastewater treatment plants are upgraded to provide biological nutrient removal (BNR), the demand for supplemental carbon and volatile fatty acids (VFAs) is growing. So, what should plant staff consider when evaluating potential sources?

BNR Basics

BNR is a two-step process: nitrification and denitrification. In the first step, ammonia-nitrogen is converted to nitrate and nitrite. In the second, bacteria oxidize simple carbon compounds — using nitrate as an electron acceptor — which ultimately converts nitrates to nitrogen gas. To maximize nitrate removal, wastewater treatment plants need a source of readily biodegradable carbon as a substrate for denitrification. The carbon could come from soluble biochemical oxygen demand (BOD) in wastewater, cell mass decay in endogenous denitrification, or a supplement.

The most commonly used BNR systems are three-stage activated sludge systems with anaerobic, anoxic, and aerated zones (see figure, p. 52). They are designed to use soluble BOD as their source of carbon. However, if a treatment plant's effluent limit is about 3 to 5 mg/L of total nitrogen, another denitrification step typically is required. A four- or five-stage activated sludge process can remove more nitrate via endogenous denitrification in a large post-anoxic zone, or a supplemental carbon source can be added to increase denitrification rates and reduce the size of the post-anoxic zones.

Tertiary fixed-film denitrification processes, such as deep-bed denitrification filters, also need a readily biodegradable carbon source.

Carbon Sources

Supplemental carbon can come from "external" sources, such as purchased chemicals, or

"internal" sources, such as fermented wastewater or sludge. Both should be carefully considered when a treatment plant needs supplemental carbon to meet nutrient limits.

When a plant must meet stringent total nitrogen limits, however, some of the denitrification typically occurs toward the end of the process — either in a post-anoxic zone in the activated sludge BNR process or in a tertiary denitrification process. Fermentate typically is not feasible here because of its nitrogen and phosphorus content, as well as its variable carbon concentration. A clean, consistent carbon source is required (see Table 1, p. 50).

Methanol. The most common external carbon source used in denitrification processes, methanol is widely available and cost-effective. However, it has several drawbacks. Methanol is highly flammable (with a flashpoint of 12°C [54°F]), so National Fire Protection Association (Quincy, Mass.) and other requirements must be met. Phosphorus-accumulating organisms cannot use it, so if a treatment plant needs carbon for denitrification and VFAs for biological phosphorus removal, methanol cannot meet both objectives. Recent research suggests that methanol is not the most efficient source of carbon for denitrification in anoxic zones with brief hydraulic residence times (HRTs) and solids retention times. Finally, the cost and availability of methanol has recently begun fluctuating widely.

So, many utilities now are considering other carbon sources.

Acetic acid. Commonly used as a VFA source for biological phosphorus removal, acetic acid also is an efficient carbon source for denitrification processes. Although less volatile than methanol, concentrated acetic acid solutions have a relatively low flashpoint and a freezing point of 17°C (62°F). So unless dilute solutions are used, the facility must meet code requirements for storage of flammable liquids and include measures to avoid freezing.

Several North Carolina treatment plants, in-

Table 1. Selected Information for Supplemental Carbon Sources

Carbon Source	Chemical Formula	Specific Gravity	Estimated COD Content, mg/L
Methanol	CH ₃ OH	0.79	1,188,000
Ethanol	CH ₃ CH ₂ OH	0.79	1,649,000
Acetic Acid (100% solution)	CH ₃ COOH	1.05	1,121,000
Acetic Acid (20% solution)	CH ₃ COOH	1.026	219,000
Sugar (sucrose) (50% solution)	C ₁₂ H ₂₂ O ₁₁	1.22	685,000
MicroC™	Proprietary product, includes 5% methanol	1.16	630,000
UnicarbDN	Glycerine based	1.09	600,000 – 1,000,000
Primary Sludge Fermentate	VFAs (primarily acetic and propionic acids)	1.0	400 – 800 (soluble COD, depending on quantity of elutriant)

cluding the McDowell Creek plant in Charlotte, have used a 20% acetic acid solution (a high-quality pharmaceutical manufacturing waste) for the past 8 years as a VFA source for biological phosphorus removal or as a carbon source to enhance denitrification in post-anoxic zones.

Sucrose solution. Sugar solutions are attractive sources of carbon because they are not safety hazards. However, they attract insects and rodents, may have variable carbon concentrations, and may not always be available (depending on the source).

Suffolk Industrial Chemicals (Suffolk, Va.) produces 25% to 50% sugar solutions for customers in North Carolina and Virginia. In 2005, Gastonia, N.C., tested a 25% sucrose solution in the post-anoxic zones at the Long Creek and Crowders Creek wastewater treatment plants. The goal was to find a less expensive alternative to the 20% acetic acid solution. Several months of testing indicated that the sucrose and acetic acid doses were comparable and produced similar treatment results. This may have resulted from the rapid breakdown of sugar to acetate in the anoxic zone.

High-fructose corn syrup. High-fructose corn syrup (HFCS) is produced when corn is wet-milled into cornstarch and then undergoes a three-step enzymatic conversion. It must be stored at high temperatures (27°C to 32°C [81°F to 90°F] at 55% fructose content), and the piping must be lagged and heat-traced to minimize the risk of cooling and crystallization.

During a recent pilot study for the Eastern Municipal Water District (Fountain Valley, Calif.), staff at the Temecula Valley Regional Water Reclamation Facility found that HFCS-42 cost about three times as much as methanol (which then cost

\$0.32/L [\$1.21/gal]). The cost depended on the dose, which averaged about 6 kg per kilogram of nitrogen under normal operating conditions (see sidebar on p. 53 for more information).

High-fructose corn syrup historically was linked to the soft drink and sugar markets, but the recent boom in ethanol production (sugarcane and corn are common feedstocks) now has tied it more closely with the petroleum market. As a result, its cost has increased by almost 50% since 2005 and is expected to be more volatile and continue rising.

MicroC. MicroC™ and MicroC G™ are made by Environmental Operating Solutions (Bourne, Mass.). MicroC is a proprietary mix of agriculturally derived compounds and 5% methanol, which lowers the freezing point and reduces the viscosity. Its chemical oxygen demand (COD) is 600,000 mg/L.

The Parkway Wastewater Treatment Plant in Laurel, Md., ran a full-scale test of this chemical in 2006. Testing results showed about 6 mg of COD was consumed per milligram of nitrate-nitrogen denitrified. The Mattabassett District in Cromwell, Conn., is successfully using MicroC to enhance nitrogen removal as part of its aggressive, operationally focused, interim nitrogen removal strategy.

Glycerol. Glycerol is a byproduct of biodiesel production, created during the transesterification process. Biodiesel is a cleaner-burning, biodegradable fuel made from renewable resources, such as vegetable oils and animal fats. When reacted with alcohol (usually methanol), such fats and oils generate biodiesel and a crude glycerol, which contains about 20% water.

As biodiesel gains popularity, more crude glycerol is being produced. At press time, the

Table 2. Selected Denitrification Kinetic and Stoichiometric Coefficients for Alternate Carbon Sources

Carbon Source	Maximum Specific Denitrifier Growth Rate		Yield, Y (g biomass COD/g sub- strate COD)	COD/NO ₃ -N Ratio
	m _{max} 1/d	Temp, °C		
Methanol ^(a)	0.5	13	0.38	4.6
	1.0	19		
Methanol ^(b)	1.3	20 (developed Arrhenius coefficient of 1.13)		
Methanol ^(d)	0.52	10		
	1.86	20		
Methanol ^(e)	1.25	20 (developed Arrhenius coefficient of 1.13)	0.4	4.79
Methanol ^(f)			0.45	
Acetate ^(a)	1.3	13	0.18	3.5
	3.7	19		
Acetate ^(b)	4.0	20		
Acetate ^(c)			0.192	3.6
Acetate ^(f)			0.18	
Ethanol ^(a)	1.2	13	0.39	4.7
	3.5	19		
Ethanol ^(b)	1.3	20		
Ethanol ^(f)			0.51	
Sugar ^(b)	4.0	20		
Sugar ^(f)			0.35	
Glucose ^(c)			0.365	4.5
<p>References:</p> <p>(a) Mokhayeri et al., 2006. (b) Dold et al., 2007. (c) Copp and Dold, 1998. (d) Tchobanoglous, Burton, and Stensel, 2003. (e) Nichols et al., 2007. (f) Adapted from McCarty, 1969.</p>				

U.S. demand for crude glycerol was about half the production rate, which has driven the price down from \$2.09/kg in 2003 to less than \$0.22/kg today.

At press time, New York City was pilot-testing it. Other facilities are testing glycerol solutions, such as Unicarb-DN.

Unicarb-DN. Unicarb-DN, made by Univar (Redmond, Wash.), consists of glycerol and additives that lower the freezing point to less than -34°C (-30°F) and the viscosity to nearly that of water. Its COD is reported to be between 600,000 and 1 million mg/L.

The glycerol comes from a biodiesel (soybean oil-based) production facility near the Univar plant outside Harrisburg, Pa. At press time, the chemical cost \$0.63/L (\$2.40/gal), and the company expects this price to remain relatively stable. It has been tested at the Mt. Airy (Pa.) Wastewater Treatment Plant, the Fort Indiantown Gap (Pa.) Wastewater Treatment Plant, and the

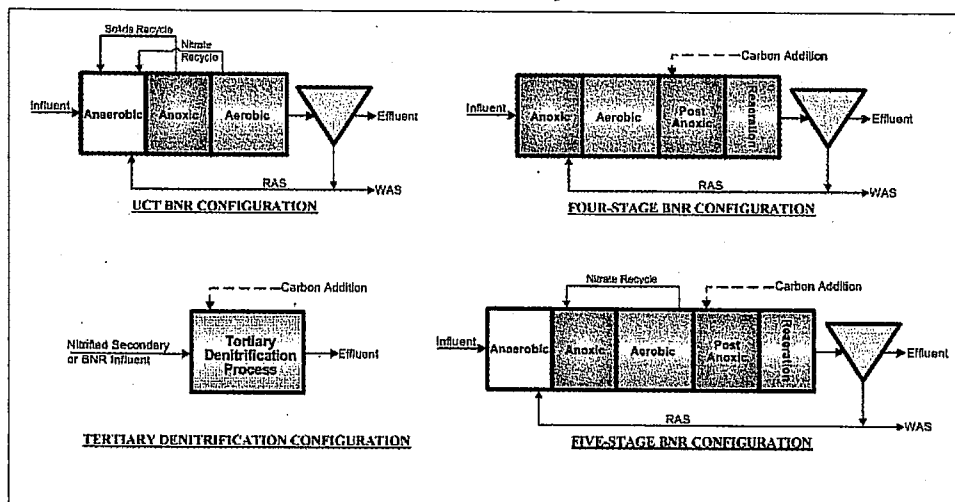
Parkway treatment plant.

Industrial wastes. Because chemical addition can be expensive, several treatment plants have considered less costly options, such as sugar, molasses, and ethanol wastes. Before “recycling” industrial carbon, however, plant staff should evaluate whether the industrial source is clean and relatively free of nutrients, metals, and other contaminants. Staff also should determine how consistent the carbon concentration is, as well as the source’s availability. The industry’s production schedule may vary according to season or demand for the primary product, so the readily biodegradable carbon byproduct may not always be available in sufficient quantities.

Carbon Needs

Several researchers have examined denitrification kinetics, carbon requirements, and cell yields. For example, P.L. McCarty *et al.* (1969) evaluated how a number of carbon sources af-

Commonly Used Biological Nutrient Removal Systems



Variables To Consider

Denitrification rates depend on the carbon source used. For example, P.L. McCarty *et al.* (1969) found that acetic acid generated higher denitrification rates than methanol did. Researchers also have determined that a special group of bacteria (called *methanol-oxidizing bacteria*, or *methylo-trophs*) use methanol for denitrification.

During the past several years, researchers at the Blue Plains Advanced

Wastewater Treatment Plant in Washington, D.C., and other treatment facilities in Maryland, Virginia, and New York have been investigating the denitrification kinetic parameters associated with methanol and other carbon sources. During the Washington, D.C., study, researchers found the maximum specific growth rate for methylo-trophs was about 1.3/d at 20°C, which is much lower than that of other heterotrophic bacteria. Ethanol had a similar growth rate. Denitrifying bacteria that used acetate and sugar, however, had a higher growth rate (4.0/d at 20°C). The research also examined the ability of different groups of bacteria to adapt to a change in the readily biodegradable carbon source. The results suggested that if the activated sludge culture primarily contained methylo-trophs, they would readily adapt to ethanol, but an acclimation period would be necessary if acetate or sugar was substituted for methanol (see sidebar on p. 53 for more information).

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$$\text{Methanol requirement} = 2.47 \text{ NO}_3\text{-N} + 1.53 \text{ NO}_2\text{-N} + 0.87 \text{ DO}$$

where

NO₃-N = nitrate nitrogen;
 NO₂-N = nitrite nitrogen; and
 DO = dissolved oxygen.

Both the amount of chemical needed for denitrification and the resulting solids production are related to the cell yield (how efficiently the bacteria convert COD into biomass under anoxic conditions). Some of the consumed COD is converted into biomass; the rest is oxidized to carbon dioxide and water. Carbon sources with high anoxic yields produce more solids; low-yield sources produce fewer solids and have lower overall COD requirements for denitrification (see Table 2, p. 51). The amount (kg) of COD required to reduce 1 kg of nitrate-nitrogen equals 2.86/(1 - yield).

Thus, the carbon source's anoxic yield coefficient affects both the amount of carbon (as COD) needed for denitrification and the amount of solids produced. However, most of the yield research to date is lab-scale. More full-scale testing of various carbon sources is needed to establish whether differences in dose requirements and solids yields significantly affect performance and cost.

The required volume for anoxic zones depends on the denitrification rate, which depends on the denitrifying bacteria's maximum specific growth rate. Typically, anoxic and post-anoxic zones with a nominal HRT of 1 to 2 hours are adequate for denitrification when readily biodegradable carbon sources, such as wastewater, readily biodegradable COD, acetic acid, and sugar, are used. However, because of the low growth rate of methylo-trophs, larger anoxic zones are needed when methanol is used as the carbon source — especially in areas where wastewater temperatures drop in winter. In other words, if acetate or sugar is used as the carbon source, the anoxic zones can be smaller than they would be if methanol or ethanol is used.

Because denitrifying bacteria attach to the carrier media, fixed-film denitrification processes

are more forgiving. For example, deep-bed denitrification filters usually operate at an empty bed HRT of 15 to 30 minutes, easily producing an effluent containing less than 1 mg/L of nitrogen oxides-nitrogen.

Adding a VFA source, such as acetic acid or sugar (which quickly converts to VFAs), to the post-anoxic zone of a biological phosphorus removal process may result in the release of stored phosphorus from the mixed-liquor suspended solids. In general, this should not be too problematic if the readily biodegradable carbon dose is controlled to maintain some residual nitrate and the reaeration zone is large enough to take up the released phosphorus.

So, design engineers and treatment plant staff should consider the denitrification kinetics data for carbon sources when sizing BNR facilities. The ability to use multiple carbon sources generally makes a BNR plant more reliable and allows operators to change sources when market conditions and costs fluctuate. When switching carbon sources, however, staff should select the initial doses carefully and monitor results to ensure that excess carbon does not break through to the effluent.

Coming Soon to a Plant Near You

As more wastewater treatment plants are upgraded to meet very low total nitrogen limits, carbon augmentation has gained widespread interest. Considering the timeline for the Chesapeake Bay and Long Island Sound nutrient-reduction programs, many treatment plants will have implemented BNR by 2014 and will be using a supplemental carbon source to achieve their denitrification goals. More research and full-scale evaluation of alternate carbon sources are needed to help plant staff make informed decisions about carbon sources and optimize BNR performance.

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