Tertiary Denitrification and Very Low Phosphorus Limits: A Practical Look at Phosphorus Limitations on Denitrification Filters

Note: This publication first appeared at WEFTEC 2006 and describes some practical operating requirements for denitrification filters. ASA has ChemScan process analyzers in operation at many of the plants discussed including HL Mooney, VA, Clark County, NV, and Hagerstown, MD.
TERTIARY DENITRIFICATION AND VERY LOW PHOSPHORUS LIMITS: A PRACTICAL LOOK AT PHOSPHORUS LIMITATIONS ON DENITRIFICATION FILTERS

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ABSTRACT

Deep-bed denitrification filters have been successfully used for over 25 years to meet total nitrogen (TN) limits of 3 mg/L and even lower. In some cases, the wastewater treatment plants (WWTPs) also have had moderate total phosphorus (TP) limits, in the range of 0.5 to 2 mg/L. More recently, some WWTPs are required to meet very low TN and TP limits simultaneously. For example, as the result of the development of total maximum daily loads (TMDL) for the Chesapeake Bay, many WWTPs in Maryland and Virginia will be required to meet limits of 3 mg/L TN and 0.3 mg/L TP on a 12-month average basis. A number of these plants have even more stringent phosphorus limits of 0.18 mg/L monthly average. This has raised practical operating concerns with respect to the ability of these WWTPs to meet low TP limits without additional treatment downstream of the filters. In addition, a certain amount of phosphorus is required to support the growth of denitrifying bacteria and it may be difficult to ensure there is sufficient phosphorus to promote denitrification if too much is removed in upstream processes. This paper will examine phosphorus requirements for denitrification, and expand upon earlier information presented at the International Water Association Biofilm Systems VI Conference in September 2006. Operating data from several full-scale and pilot denitrification filters operating for low TN and TP simultaneously will be presented and evaluated to determine when low phosphorus concentrations actually impact denitrification, and identify strategies for ensuring reliable performance.

KEYWORDS: Denitrification filters, phosphorus limitations, phosphorus release

INTRODUCTION

Deep-bed denitrification filters have been successfully used for over 25 years to meet effluent total nitrogen (TN) limits of 3 mg/L and even lower. More recently, some facilities are required to meet very low TN and total phosphorus (TP) limits simultaneously. For example, as the result of water quality concerns for the Chesapeake Bay, many wastewater treatment plants (WWTPs) in Maryland and Virginia will be required to meet limits of 3 mg/L TN and 0.3 mg/L TP on a 12-month average basis, and some WWTPs have even more stringent phosphorus limits of 0.18 mg/L monthly average. This has raised practical operating concerns about potential limitation of biological growth in the filters if too much phosphorus is removed in upstream processes.

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To examine the impact on denitrification performance, simultaneous phosphorus precipitation and denitrification was tested using upflow filters in the Stockholm area (Hultman et al, 1994; Jonsson et al, 1997; Jonsson, 1998). It was estimated that under the conditions tested, a phosphorus concentration of 0.1 mg/L was sufficient for denitrification. At reduced concentrations of 0.03 mg/L PO4-P, denitrification performance was impacted. Similar concerns of phosphorus limitation have been discussed for separate stage nitrification processes that follow chemically enhanced primary settling. For example, testing conducted by Nordeidet et al (1994) showed that tertiary nitrification in rotating biological contactors was impacted at phosphorus concentrations below 0.15 mg/L PO4-P. These results illustrate the potential difficulty of operating denitrification filters to meet low nitrogen and phosphorus limits simultaneously.

**How Much Phosphorus Is Needed For Denitrification?**

The denitrification process consists of biological oxidation of the influent chemical oxygen demand (COD, in most cases methanol) using nitrate and nitrite as the oxygen source. The COD is used for cell growth and respiration and a specific amount of phosphorus is required. The literature suggests that 0.022 g TP is required per g biomass COD. For example, using a filter influent NO3-N concentration of 6 mg/L, a methanol dosage ratio of 3 g per g NO3-N, and a corresponding COD to methanol ratio of 1.5, the readily biodegradable COD would be 27 mg/L. The biological yield coefficient for denitrification using methanol is estimated at 0.4 g biomass COD per g COD oxidized (Copp & Dold, 1998). Applying this yield coefficient and the biomass P requirement to the influent COD of 27 mg/L results in a P requirement of 0.24 mg/L for denitrification. This can be expressed as 0.009 g P/g COD removed or 0.04 g P/g NOx-N removed. Therefore the level at which P becomes limiting depends on the amount of nitrate to be denitrified in the filters.

**WWTPs OPERATING WITH CHEMICAL PHOSPHORUS REMOVAL UPSTREAM OF DENITRIFICATION FILTERS**

A number of WWTPs use metal salts to precipitate phosphorus upstream from the denitrification filters. This may provide a degree of control over the actual TP concentration entering the filters through adjustment of the chemical dosage. However, the precipitated P is almost completely settled out in the clarifiers and is not available for bacterial growth in the filters. Results from two plants operating chemical phosphorus removal processes upstream from denitrification filters are summarized below.

**Fiesta Village Advanced WWTP, Florida**

The Fiesta Village AWWTP in Florida has operated deep-bed Tetra DENITE® filters to meet an effluent TN limit of 3 mg/L for many years and has daily maximum and monthly average TP limits of 1 and 0.5 mg/L, respectively (Meyer, 2005). Alum is added to the oxidation ditches for chemical phosphorus removal upstream from the filters. Some denitrification is achieved in the activated sludge process, and the nitrate concentrations in the filter influent range from 1.5 to 4 mg/L. Fiesta Village typically meets less than 0.2 mg/L TP monthly average while achieving less than 2 mg/L TN. The plant does not use online nutrient monitoring and controls chemical
feed manually, but does not have any difficulty with P limitation in the filters at their typical nitrate loadings.

**H.L. Mooney WWTP, Virginia**

The H. L. Mooney Advanced Wastewater Treatment Plant has a design capacity of 18 mgd with in-line diurnal flow equalization and an activated sludge process that can be operated in either a MLE or step-feed nitrification/denitrification configuration. Ferric chloride is added ahead of both the primary and secondary clarifiers for phosphorus precipitation. Deep bed Tetra DENITE® filters are provided for additional denitrification and suspended phosphorus removal. Nutrient effluent limits are currently 8 mg/L TN and 0.18 mg/L TP. Effluent TN limits are in the process of being changed to an annual average concentration limit of 3 mg/L.

The denitrification filters have been in service since 2003, but have only been operated in denitrification mode during three relatively short testing periods. Because of the low total phosphorus effluent discharge limits that must be met, the secondary effluent TP concentration fed to the denitrification filters is normally less than 0.15 mg/L and the ortho-phosphorus (OP or soluble P) concentration is normally less than 0.05 mg/L. Since all of the phosphorus removal is accomplished with chemical precipitation, there is very little phosphorus in the filter feed water that is bio-available to support growth of denitrifying bacteria in the filters. In fact, the low phosphorus concentration was likely a significant factor in the difficulties the plant experienced during initial denitrification startup of the filters. The initial denitrification start-up of the filters took six months (December 2003 through June 2004) with methanol feed and seeding with mixed liquor from the activated sludge process to consistently achieve filter effluent TN concentration of less than 3 mg/L.

Operational data from two additional denitrification testing periods in March through April 2005 and December 2005 through January 2006 were studied to evaluate potential impacts of the low available phosphorus on denitrification performance. Data for the December 2005 – January 2006 testing period are shown in Figure 1. Methanol feed was initiated on 12/12/05 with the secondary effluent NOx-N concentration averaging less than 4 mg/L. By 12/19/05, filter effluent NOx-N concentrations were consistently being reduced to less than 1 mg/L. On 1/10/06 adjustments were made in the methanol feed rate to the anoxic zone in the activated sludge process to increase the NOx-N concentration in the feed water to the filters by about 2 mg/L. The increased nitrate loading to the filters resulted in an increase in filter effluent NOx-N concentration to almost 3 mg/L and continued to fluctuate above 1 mg/L in response to fluctuations in filter influent NOx-N concentration. Soluble OP concentrations in the filter feed water were below the laboratory test method detection limit of 0.05 mg/L throughout the testing period. Any time the OP:NOx-N ratios in the filter influent wastewater fell below 0.01, the filter effluent NOx-N concentration rose above 1 mg/L. Because of the analytical detection limits for measuring OP concentrations below 0.05 mg/L and the relatively low NOx-N concentrations in the filter feed water during this testing period, the accuracy of the OP:NOx-N ratio threshold at which phosphorus may have affected denitrification performance may not be precise, but the data indicates that the filter was operating near the threshold.
The other testing period evaluated for the H. L. Mooney denitrification filters occurred during March and April 2005. This testing period was conducted during recovery from loss of nitrification in the activated sludge process when all of the anoxic zone reactor volume was temporarily converted to aerated service to help re-establish full nitrification. In order to continue to comply with current discharge permit nitrogen removal requirements, the filters were operated in denitrification mode with methanol addition. Figure 2 shows the filter operating data during a period of increasing NOx-N loading followed by a period of steady-state operation at normal NOx-N loadings. During the period of rapid increase in the filter feed NOx-N concentration, the filter effluent NOx-N concentration also increased, but a significant amount of nitrate reduction was achieved by the filters. The amount of nitrate reduction that occurred during this period may have been limited by the amount of phosphorus needed to support the rapid growth of biomass in the filter in response to the increasing NOx-N loading. Soluble OP in the filter feed water remained below the analytical detection limit of 0.05 mg/L during the period of increasing NOx-N loading. The OP:NOx-N ratio during this period dropped from 0.05 to less than 0.005 and the filter effluent NOx-N concentration increased from 1 mg/L to over 6 mg/L. Once nitrification was fully recovered, the anoxic zones in the activated sludge process were re-established and NOx-N concentration in the filter feed water dropped back about 4 mg/L. As the NOx-N loading on the filter stabilized, the OP:NOx-N ratio in the filter feed water increased to over 0.01 and filter effluent NOx-N concentrations dropped to nearly zero.
Figure 2. H. L. Mooney Denitrification Filter Under Variable Nox-N Loading

WWTPs OPERATING WITH BIOLOGICAL PHOSPHORUS REMOVAL UPSTREAM OF DENITRIFICATION FILTERS

Plants operating for biological phosphorus removal (bioP) upstream from denitrification filters may be at a disadvantage in that phosphorus removal is more likely to be variable. In addition, excellent performance can result in secondary effluent OP concentrations of below 0.10 mg/L and could limit tertiary denitrification performance. However, the biological solids entering the filter contain phosphorus accumulating organisms (PAOs) that store excess P. Typical TP/TSS ratios for activated sludge solids are less than 2%, but the TP/TSS ratio for biological solids containing PAOs are often 5% or greater, which corresponds to about 0.5 mg/L TP if the filter influent TSS is 10 mg/L. The PAOs can release this stored P under anaerobic and anoxic conditions, and through cell decay. This can be problematic or may offer an advantage, depending on the treatment goals. Operating considerations for several plants are discussed below.

Clark County Water Reclamation District, Nevada

The Clark County Water Reclamation District in Las Vegas, Nevada operates a 100 mgd biological phosphorus removal plant with chemical trim. At the current plant flows the TMDL for phosphorus translates to an effluent concentration of 0.25 mg/L. In anticipation of even more
stringent phosphorus limits, the plant staff tested operation to achieve effluent phosphorus concentrations of less than 0.05 mg/L (Drury et al, 2005). This effort included development of a plant-wide management strategy to optimize phosphorus removal to achieve the lowest possible effluent TP concentration. Once the activated sludge process started achieving the very low OP concentrations, it was noted that the phosphorus concentration was slightly increasing through the filters as shown in Figure 3 below. This was resolved in part by backwashing the filters more frequently to decrease the time that solids are stored in the media in order to minimize secondary release of phosphorus in the filters. In addition, about 4 mg/L of alum is added to precipitate any OP that is released in the filters. The plant effluent OP concentration averaged 0.02 mg/L during 2005.

Figure 3. Clark County Water Reclamation District Effluent OP Concentrations, Before and After Filtration

The Clark County results show that phosphorus release from solids can occur in filters and illustrates this phenomenon at low OP concentrations without being impacted by denitrifying bacteria taking up this released phosphorus for biological growth. This phosphorus release likely occurs to some extent through endogenous decay of secondary effluent but would be more pronounced in a secondary effluent where phosphorus accumulating organisms from a bioP process are present.
Truckee Meadows Water Reclamation Facility, Nevada

The Truckee Meadows Water Reclamation Facility in Reno, Nevada operates an activated sludge biological nutrient removal process followed by nitrification biotowers, fluidized bed denitrification reactors and gravity filters. Since nitrification is accomplished in a separate stage process, nitrate concentrations entering the denitrification units typically range from 20 to 30 mg/L. The denitrification process operation is excellent and effluent NO₃-N concentrations have averaged below 0.5 mg/L for many years. The OP concentration entering the denitrification process is typically 0.25 to 0.35 mg/L. The plant staff has found that if OP concentrations drop below 0.25 mg/L, the plant experiences phosphorus limitations in the denitrification process (Gray, 2006). Under these conditions, phosphoric acid is dosed to the denitrification influent wastewater to increase the soluble phosphorus concentration. This occurs three or four times a year for a few days. Based on this information, it is estimated by the authors that the threshold for phosphorus limitation on denitrification occurs at denitrification process influent OP/NOₓ-N ratio of 0.01. The final effluent TP and NO₃-N concentrations have been consistently excellent and monthly average data for the last several years is shown in Figure 4.

Figure 4. Truckee Meadows Water Reclamation Facility Final Effluent NO₃-N and TP Concentrations

Hagerstown, Maryland Denitrification Filter Pilot

The Hagerstown WWTP operates an activated sludge BNR process for partial denitrification and biological phosphorus removal. Pilot testing of upflow continuous backwash filters was conducted as part of a study to evaluate options for upgrading the plant to meet the State of
Maryland enhanced nutrient removal limits of 3 mg/L TN and 0.3 mg/L TP. The results of this pilot testing are discussed in detail in Schauer (2006). One of the testing objectives included assessing whether reliable denitrification could be maintained at low influent OP concentrations. A detailed discussion of the apparent phosphorus requirements for denitrification is provided in deBarbadillo et al (2006) and is also summarized below.

The denitrification filter pilot was tested in several phases, including operation at both constant hydraulic loading rates and under diurnal flow variations. In general, the secondary effluent TP and OP concentrations were often less than 0.5 and 0.1 mg/L, respectively. Denitrification performance was also tested with simultaneous precipitation of phosphorus using ferric chloride, and phosphoric acid was dosed to the filter influent to increase the OP during this phase.

Since the Hagerstown WWTP operates an activated sludge BNR system for partial denitrification and biological phosphorus removal, the NOx-N loading to the filters was relatively low. At the typical filter influent NOx-N concentrations of 6 mg/L, and without phosphoric acid addition, virtually all of the NOx-N was denitrified and the low influent and effluent soluble phosphorus concentrations did not seem to impact denitrification performance.

To examine filter performance under higher nitrate loading rates and provide an opportunity to examine potential phosphorus limitation in more detail, sodium nitrate was dosed to the pilot influent wastewater to increase the nitrate loading (Figure 5). During the first period of testing with supplemental nitrate (Phase A), no additional phosphorus was added to the influent. The filter effluent OP concentration was at or near the detection limit of 0.01 mg/L during this phase, while the effluent NOx-N concentration averaged about 7.1 mg/L. The combination of the high effluent NOx-N concentration and extremely low effluent OP concentration suggested that either the maximum nitrate removal capacity of the pilot filter had been reached, or that the low phosphorus concentration was limiting the growth of the bacteria required for denitrification.

**Figure 5. Observed Phosphorus Limitations During Operation at High Nitrate Loading**
To determine whether phosphorus was limiting denitrification performance, phosphoric acid was added to increase the influent OP concentration during Phase B. The target filter influent NOx-N concentration was reduced from 14 to about 9 mg/L to preserve the remaining stock of sodium nitrate for additional testing. When the soluble phosphorus in the filter influent was increased, the effluent NOx-N concentration steadily decreased over a period of three days until the target NOx-N concentration of approximately 1 mg/L was reached.

Once the effluent NO₃-N dropped below 1 mg/L, the target influent NOx-N concentration was increased from 9 mg/L to approximately 16 mg/L and phosphoric acid addition was continued. The filter effluent NOx-N concentration initially rose to about 4 mg/L in response to the higher nitrate loading, but dropped to about 2 mg/L by the end of the second day at the higher loading. Phosphorus was not limiting during this phase and after the first day of operation at this higher NOx-N loading rate, there was very little change in denitrification performance.

During the course of the testing there was concern that the low soluble phosphorus concentrations would be inadequate to support the required denitrification. However, with the exception of the testing at high nitrate loadings, denitrification performance was excellent and did not appear to be impacted by the low phosphorus. To examine the impact of soluble phosphorus on denitrification performance, the ratio of influent OP to NOx-N was plotted against the effluent NOx-N concentration as measured in the laboratory composite samples (Figure 6). The resulting graph and inset with expanded x-axis suggest that the low influent OP did not result in elevated NOx-N concentrations until the OP/NOx-N ratio was reduced to about 0.01, which is well below the theoretical requirement of 0.04 g P/g NOx-N denitrified.

**Figure 6. Impact of Influent OP to NOx-N Ratio on Denitrification Effluent NOx-N**
A similar plot of the filter influent OP/NO\textsubscript{3}-N ratio was prepared using online nutrient monitoring data. The online analyzer measured nutrient concentrations approximately four times per hour and provided additional information at variable influent OP and NO\textsubscript{x}-N concentrations. However, although there was a slight increase in scatter in the data, the online data again showed that the low influent OP did not result in elevated NO\textsubscript{x}-N concentrations until the OP/NO\textsubscript{x}-N ratio was reduced to 0.01 to 0.02.

In addition to examining phosphorus requirements in terms of an OP/NO\textsubscript{x}-N ratio, phosphorus removal was also compared with COD removal performance. Based on an expected net yield of 0.4 g biomass COD per g of COD removed and a normal biomass phosphorus content of 0.022 g/g COD, we would expect to require about 0.009 g of OP per g of COD removed. The actual OP removal was generally less than 0.005 mg OP per mg COD removed and averaged about 0.002 mg OP per mg COD removed without causing the filter effluent NO\textsubscript{x}-N to rise above the treatment target of 1 mg/L.

Because of the consistent denitrification performance even when the available phosphorus concentration appeared to be insufficient for biological growth, it is suspected that the balance of the phosphorus requirement was being met with phosphorus released from PAOs in the secondary effluent, or from cell lysis. Although these individual contributions could not be measured directly, these phenomena likely impacted denitrification in a positive manner. Consistent with the presence of PAOs, the filter influent TP/VSS ratio averaged 10.8 percent. The backwash solids included PAOs from the plant and filter biomass. The TP/VSS ratio of the backwash solids averaged 5%, or less than half that of the filter influent solids. It was concluded that denitrification filters could be operated reliably to meet the Maryland ENR limits of 3 mg/L TN and 0.3 mg/L TP, and that phosphorus release from the PAOs in the secondary effluent to the filters helped prevent phosphorus limitations.

PRACTICAL IMPACTS OF OPERATION OF DENITRIFICATION FILTERS AT WWTPS WITH LOW PHOSPHORUS LIMITS

Meeting very low TP limits while operating denitrification filters is complicated by the need for sufficient phosphorus to sustain biological growth. A review of operating data suggests that the risk of phosphorus limitations is probably minimal if only a few mg/L of nitrate are to be denitrified, but is a real concern at nitrate concentrations above approximately 10 mg/L as suggested by some of the data from H.L. Mooney WWTP, Truckee Meadows WRF and the Hagerstown pilot. Thus, phosphorus limitations may be less likely to impact WWTPs that are operating BNR processes to reduce TN before the filters since the amount of nitrate to be denitrified, and the corresponding phosphorus requirement, are reduced.

Data from the H.L. Mooney facility, Truckee Meadows WRF and the Hagerstown pilot all suggest that the threshold for phosphorus limitation on denitrification occurs at a filter influent OP/NO\textsubscript{x}-N ratio of approximately 0.01. At ratios of 0.02 and higher, denitrification does not appear to be impacted even though this is below the estimated requirement of 0.04 OP/NO\textsubscript{x}-N. This difference may be made up in part by release of phosphorus from secondary effluent solids captured in the filters, phosphorus release from any PAOs and decay of denitrifying biomass.
Phosphorus release in the filters from PAOs present in the secondary effluent solids from biological phosphorus removal processes may help denitrification but potentially can negatively impact the ability of the plant to meet very low TP limits without having an additional chemical precipitation step.

From the data presented herein, it is estimated by the authors that denitrification filters can be operated successfully to meet effluent TN limits of 3 mg/L while also meeting TP limits as low as 0.15 to 0.2 mg/L. If necessary, chemical polishing of phosphorus can be performed simultaneously by added a metal salt to the filter influent wastewater. If there is a need to reach lower effluent TP limits, the advantages and disadvantages of this and other options merit serious consideration.

Inclusion of a phosphoric acid feed system for intermittent use when phosphorus concentrations are too low to support adequate denitrification may be worthwhile. Operating experience at the Truckee Meadows facility shows that this strategy can be used reliably.

Operation for very low TN and TP limits requires a level of monitoring and control that would be time consuming to perform manually. Therefore, the use of reliable online instrumentation and automatic chemical feed control is needed for both phosphorus control and methanol dosing to the filters.

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