An introduction to optimizing supplemental nutrients at pulp and paper wastewater treatment plants

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ABSTRACT: Development and maintenance of mill- and wastewater treatment system-specific programs aimed at optimizing use of supplemental nutrients for purposes of minimizing residual nutrients in treated effluents have evolved in recent years and are summarized. Suggestions for monitoring of nutrient forms in wastewaters prior to and during biological treatment are presented, as are approaches for determining supplemental nutrient requirements, monitoring biomass characteristics, and achieving minimum nitrogen and phosphorus residuals in treated final effluents while maintaining targeted levels of biological treatment. Aspects of nutrient management relevant to activated sludge (AS) and aerated stabilization basin (ASB) systems are presented, and ASB configurations operated in part to minimize nutrient levels in treated effluents are highlighted.

Application: For mill personnel, this is an introductory overview of considerations and approaches for managing nutrients in pulp and paper wastewater treatment plants. It will be useful to those interested in optimizing the use of supplemental nutrients and/or minimizing nutrient residuals in treated effluents while maintaining treatment plant performance for biological oxygen demand (BOD) and solids removal.

In the United States, a great number of waterbodies are considered to be impaired due to the presence of excess phosphorus (P) and nitrogen (N). These nutrients play an important role in aquatic systems but when present in excess can contribute to nuisance algae conditions or, in the extreme, disrupt ecological balances of periphyton, benthic invertebrates, and/or fish communities [1,2]. Contributors to nutrient-related degradation of streams can include runoff from urban, residential, and agricultural land (so-called "non-point" sources) as well as discharges of treated municipal and industrial wastewaters (i.e., "point" sources). The relative significance of nutrient contributions to a stream, lake, or estuarine system varies considerably, but in many watersheds non-point sources are the principal anthropogenic source of nutrients. Nonetheless, point sources of nutrients are closely scrutinized by regulatory authorities because of their sometimes significant contribution, relative ease of measurement, and the existence of a governing system for implementing reduction mandates.

The nutrients N and P often do not occur in pulp and paper mill process wastewaters at levels sufficient to support adequate biological treatment of organic matter present in the wastewater. Therefore, it is common practice for mills to provide supplemental nutrients prior to or during biological treatment. Nutrient supplementation, when necessary, is a challenging proposition wherein sufficient nutrient must be made available to support the biological activity needed to accomplish treatment of wastewater, but not in unnecessarily excessive amounts that would increase costs and the level of nutrient residuals in treated effluents.

The objective of this article is to provide an introduction to practices that, when used appropriately in a mill- and treatment system-specific program, will help optimize use of supplemental nutrients and minimize nutrient residuals in treated effluent. The information provided is intended to be neither a comprehensive review of all options available for nutrient management nor a detailed "how to," but rather suggestions, based on the published literature and authors' experiences, that may offer avenues to improve existing wastewater treatment system operational practices with respect to nutrient management.

SOURCES AND FORMS OF NUTRIENTS IN MILL WASTEWATERS

Sources of nutrients

Mill wastewaters tend to lack N and P in amounts needed to support biological treatment, but they are not devoid of these nutrients. For example, raw effluent from an integrated bleached kraft mill was reported as having a BOD_5:N:P ratio of 100:1.2:0.2 (BOD_5 = amount of dissolved oxygen consumed in five days by biological processes breaking down organic matter) [3]. N and P enter mill operations with fuels, fibrous raw materials, freshwater, and certain process additives.

Fuels such as bark and coal burned in mill boilers contain nutrients. N is largely lost in gaseous forms with boiler exhaust, but P is concentrated in the ash. The P content in ash from 13 boilers burning bark or other wood residue was found to range widely, from 0.03% to 1.4%, with a median of 0.48% [4]. Ash can contribute P to wastewater in situations where it is sluiced to the sewer or where water that has contacted ash, such as wet scrubber blowdown or ash pond decantate, is sent to sewer.

As living organisms, trees utilize N and P and thus these elements enter pulp mills with the wood supply. The N content of wood varies by species and has been reported to range from 0.042% to 0.25% [5]. Most (70% to 90%) of the N in wood passes to black liquor during kraft pulping. Some is later found, as ammonia, in process condensates. If condensates are not stripped before being sewered, they can represent the single largest contribution of N to the wastewater treatment system.

The P content of stemwood has been reported to range from 0.001% to 0.01%, and levels in bark are 3 to 10 times higher [6]. The fate of P in wood during pulping and bleaching has not been widely studied. One investigation showed that 80% of P was released as orthophosphate from the first (acid) bleaching stage [7]. Residues from kraft chemical recovery (grits, dregs, lime mud) contain P, reported in the range of 0.013% to 0.57% [4], and a portion of this nutrient may become available should these residues be sluiced to primary clarification either as a regular means of management or intermittently to adjust wastewater pH.

Numerous chemical additives are used by mills to aid fiber and liquor processing, to improve paper properties, and to sustain general mill operations. Certain types of additives can contain N and/or P. Among these are defoamers, water conditioning chemicals (such as scale inhibitors), biocides, retention and drainage aids, dyes and pigments, and cleaning agents. As an example, one review of process additives found the N content of biocides to average 15% but none contained P [8]. N and P levels in process chemicals and the availability of these nutrients to be used by biomass during wastewater treatment are variable, so their reliability as nutrient sources for the wastewater treatment system is product- and system-specific [9].

Overall, nutrients from process sources can represent a significant fraction of the total nutrient requirement for wastewater treatment, and nutrient management programs should account for this contribution. Less commonly, process sources may contribute nutrients in amounts exceeding those needed for effective biological treatment; in such cases minimizing these sources may represent the primary means for minimizing residual nutrients in treated effluent.

Forms of nutrients

While it is common for nutrients to be measured and reported as "total" N and P (i.e., TN and TP), effluents are also characterized according to the chemical and physical components of these aggregate parameters. Descriptors include particulate or soluble, organic or inorganic, and bioavailable or non-bioavailable; and combining these terms for a more detailed description of nutrient forms is common. The particulate vs. soluble categorization is operational in practice based upon fractioning through a specified filter pore size. The size of the filter is conventionally specified as 0.45 µm; however, in order to maintain continuity with other particulate measurements it may be beneficial to use the same filter pore size for categorizing nutrients as that used for measuring effluent suspended solids. Regardless of the filter size, it should be recognized that the terms "soluble" and "particulate" are relative and some researchers suggest that "truly" soluble components pass through a 0.10 µm pore size filter and compounds residing between this pore size and 0.45 µm are better classified as colloidal [10].

Bioavailability is a term that attempts to characterize the portion of nutrients that are readily useable by treatment plant biomass. The chemical forms present in process wastewaters depend on mill-specific operations, but typically both organic and inorganic forms of N and P are present. Inorganic soluble forms of both N and P are generally considered to be the most bioavailable, but some organic substances can contain N (e.g., urea) or P accessible to biomass [11].

NUTRIENT BALANCES AND NUTRIENT DEMAND

Estimating the need for, and amounts of, supplemental nutrients required to support biological treatment of wastewater is not a simple matter. Factors such as variability in nutrient contributions from mill process wastewaters, variability in biological oxygen demand (BOD) load to the treatment system, recycle of nutrients within biologically active areas of the system, variable needs for nutrients by biomass, the potential for N to be "fixed" from the atmosphere by certain bacteria, and a host of other factors influence demand for supplemental nutrients and are discussed at length elsewhere [11,12,13]. However, the nutrient demands specific to each system can be approximated sufficiently for purposes of initial estimation of supplemental nutrient requirements through an improved understanding of nutrient levels in main inputs and outputs of water and solids around a treatment system.

Measurements made to estimate system inputs and outputs for nutrients are best done using total nutrient measurements (TN and TP), but should be augmented with data for soluble inorganic nutrients as a first estimate of bioavailable forms. In activated sludge (AS) systems, wasted biomass will represent a significant output, while return of filtrate from residuals dewatering systems can represent a significant nutrient input.

A first approximation of the demand for nutrients in wastewater treatment may be made using the BOD load to biological treatment and information about bacterial cell composition. In biological systems, nutrient demand has historically been tied to the classic "rule-of-thumb" BOD:N:P loading ratio of 100:5:1. This relationship is based on the elemental composition of freshwater bacterial cells (though not necessarily those specific to pulp and paper treatment systems) and the yield of cells per unit of BOD consumed. For cells with approximately 12% N and 2% P [14] and using a typical cell yield in the range of 0.4-0.5, the stoichiometry results in the 100:5:1 relationship for BOD:N:P. Supplemental addition rates for nutrients are nearly always lower than this ratio due to the availability of nutrients in incoming process wastewater, recycling of nutrients within the biologically active zones of the treatment system, and the ability of some biomass components to adapt to lower levels of N and P [15,16]. Regardless of the stoichiometry inherent in a given system, it is clear that in-mill activities to reduce BOD in untreated wastewaters will, other factors remaining constant, reduce the amount of supplemental nutrients needed.

Nutrient surveys around aerated stabilization basin (ASB) systems are more difficult to interpret than those for AS systems. Factors complicating nutrient balances for ASBs include comparatively longer hydraulic retention times relative to AS systems; that feedback of nutrients from settled (i.e., benthic), degrading biomass is spatially, temporally, and thermally variable; and that N fixation has been shown to occur in some systems, thereby adding the atmosphere as a potential source of N [11,17,18]. For these reasons, attempting to achieve a nutrient balance around an ASB can require more extensive monitoring over longer periods compared to an AS system. Computer modeling is one method that can be used to improve the understanding of nutrient dynamics in these systems [18,19] and the benefit to be gained, if any, from supplemental nutrient addition.

MANAGING SUPPLEMENTAL NUTRIENT ADDITION

There is no incentive for mills to use supplemental nutrients other than to support biological treatment at a level consistent with effluent quality targets. A balance between minimum supplemental nutrient addition and adequate biological treatment is usually achieved by targeting nutrient concentrations at a location in the treatment system that corresponds to the presence of adequate nutrient levels in the biologically active portion of the system [11]. The generally preferred approach is to measure the bioavailable forms at a location where bacteria are actively consuming BOD but after a significant portion of the inlet BOD has been consumed (e.g., in an aerated zone located in the latter portion of the basin or immediately following aeration). However, in some systems surrogate sampling locations can be used, preferably when correlations between the surrogate site and target process conditions are demonstrated to be reliable under both normal and abnormal (i.e., upset) conditions.

Orthophosphate is the most readily bioavailable form of P and under most circumstances for N it is ammonia [11,20]. However, overfeeding of supplemental N can result in nitrification yielding measurable nitrate concentrations. Historical practice has been to measure dissolved inorganic nutrients, as these are known to be bioavailable. As noted earlier, however, a portion of nutrients bound to organic substances or particulates may become bioavailable in the biologically active zones of wastewater treatment systems and for purposes of monitoring nutrients in untreated wastewater or in biologically active zones, mills should consider measuring TN and TP as well. In ASBs, the longer hydraulic time relative to AS systems may contribute to a greater availability of organic and/or particulate bound nutrients. If both dissolved inorganic and total nutrients are measured, the former may be considered a low-bias estimate of nutrient availability while the latter would be considered the upper bound estimate of availability.

Most mills carry out their process control activities by collecting grab samples and conducting ammonia and orthophosphate analyses on filtered samples. An alternative to manual sampling is to employ online nutrient analyzers, which have been used particularly in AS systems where variations in inlet loads can necessitate rapid changes in supplemental nutrient feed rates. In pulp and paper applications, however, automated analyzers have tended to have operational problems, including excessive maintenance and calibration requirements, and use of such equipment is rare at North American mills [11].

Activated sludge systems

In AS systems, the amount of biomass and conditions for biomass growth are more tightly controllable than in ASBs, and thus the need for supplemental nutrients are more predictable. In an AS system it is recommended that samples intended for nutrient monitoring be taken from the aeration basin, usually near its exit, or between the aeration basin and secondary clarification. Because P and N can be released in a secondary clarifier, creating higher residuals than are found in the aeration tank, sampling within the clarifier or after clarification is generally not advised for process control [8,21]. Historical target values reported in the literature for samples taken after the aeration tank range from 0.25 to 1.0 mg/L for orthophosphate and from 1.0 to 1.5 mg/L for ammonia [22]. A few mills with AS systems, however, have had to maintain orthophosphate residuals above 1.0 mg/L in order to avoid treatment plant upset [11]. On the other hand, a survey of nutrient management at numerous mill AS systems showed that some facilities are employing targets as low as 0.1 mg/L for orthophosphate and 0.2 mg/L for ammonia [11].

Choosing a monitoring frequency involves establishing a balance between the costs and labor for nutrient analyses, response of the supplemental nutrient delivery system to affect observed nutrient levels at the chosen monitoring location, and the objective to minimize excessive nutrient residuals in treated effluent. Monitoring frequencies are best determined on a case-by-case basis, but because of the tighter degree of control and shorter hydraulic retention time associated with AS systems, frequent monitoring (e.g., one to three times per day) and associated adjustments in supplemental nutrient feeds are usually required to achieve minimum nutrient concentrations in treated effluents.

Aerated stabilization basin systems

Supplemental nutrient addition rates, when needed, are lower for ASBs than for AS systems largely because there is not the nutrient removal mechanism in an ASB that there is with an AS; that is, biomass is not wasted on a regular basis as it is in AS systems. In most ASBs, solids accumulate within quiescent areas of the aerated basin and within any subsequent polishing ponds. Much of the bioavailable N and P initially taken up by biomass is released as the biomass solids biodegrade in these quiescent areas (often referred to as “benthic feedback”). The location(s) of accumulated solids, and thus the locations of nutrient feedback, are greatly affected by the pattern of surface aerator and/or mixer placement. Nutrients entering an ASB system eventually will leave mostly in the effluent. Bryant [23,24] indicates that typically only about 5% of N and about 20% of P are permanently captured in settled solids. Other complexities affecting nutrient requirements in ASBs include gradients in basin biological activity, available substrate, dissolved oxygen, temperature, and, especially in colder climates, thermal profiles (with benthic feedback of nutrients more pronounced in warmer months). Thus, it is not prudent to suggest a single nutrient residual target applicable to all ASBs. Rather, target residuals should be developed over time with particular attention given to the form of nutrients measured (total or dissolved inorganic), location of sample collection, season of the year, and consistency of aeration/mixing ahead of the selected sampling location.

For ASB systems that are configured and operated without features specifically associated with nutrient control (see following section on ASB designs for minimizing nutrient discharges), selection of a monitoring point should consider the location of benthic feedback of nutrients in relatively quiescent areas of the basin. Nutrients sourced from benthic deposits located in quiescent areas near basin discharge points are not available for efficient use by biomass treating BOD, and thus residuals measured in these zones may not correlate well with nutrient availability in the more biologically active zones of the basin. Under such circumstances, and where access for sample collection is convenient, one approach is to measure nutrient residuals near or at the back of the intensely aerated section. Sampling at a mid-point location, described ideally as the point where approximately two-thirds of the BOD has been removed, is the approach employed at several mill ASBs [23].

For ASBs, which respond more slowly to inlet load changes and nutrient availability than do AS systems, sampling frequencies for nutrient residuals are typically in the range of once per day to once per week, with the more frequent monitoring levels more appropriate for basins with shorter hydraulic retention times. For systems in which N fixation controls the levels of N in the system, monitoring may be unnecessary because the population of N fixing bacteria can auto-regulate concentrations.

MINIMIZING NUTRIENTS IN TREATED EFFLUENT DISCHARGES

Short of applying tertiary treatment processes such as denitrification or P coagulation to remove a portion of nutrients prior to effluent discharge [25], minimizing nutrient discharges is generally achieved though maximizing the efficiency at which available nutrients, either native or supplemental, are used by the biomass.

Activated sludge systems

In AS systems, managing supplemental nutrient addition is key to minimizing the release of soluble nutrient forms, and managing suspended solids is key to minimizing release of nutrients in particulate form. In managing soluble nutrients, wastewater treatment plant operators compare the level of residual nutrient against a target value(s) and the nutrient supplementation rate is adjusted accordingly and by an amount based on prior experience. The choice of target value(s) is system specific and will vary based on the choice of sampling location, but ultimately the target value should correlate to a combination of minimum soluble nutrient residual in the effluent and desired plant operating characteristics, especially those related to biomass settling behavior and BOD removal. Some mills use statistical process control, advisory (expert system) software, or other algorithms to decide when to adjust supplemental nutrient feeds and by how much [26,27,28]. Biomass characteristics that may indicate nutrient deficient conditions are summarized later in this article.

There are limited reports in the literature of experimentation with the use of N fixing bacteria as a means of satisfying nitrogen demand [29,30]. However, the authors are not aware of any routine use of fixation as a primary N source in pulp and paper industry AS systems. As discussed below, fixation is used at some industry ASBs.

Certain characteristics related to the design of AS systems can favor production of treated effluents with low levels of TN and TP. These include a preceding stage such as an equalization basin that dampens the variability in composition and flow of incoming wastewater; longer sludge ages and longer hydraulic residence times in aeration tanks; and secondary clarifiers of sufficient size to adequately remove even solids that settle poorly [11,31,32].

Aerated stabilization basin systems

Minimizing use of supplemental nutrients and nutrient residuals in ASB effluents can be accomplished not only though use of proper system monitoring, but also by manipulating the operational strategy or system configuration with regard to wastewater feed point(s), flow pattern, and/or aerator or mixer placement. Alternative configuration strategies targeting nutrient minimization are designed around one of two general observations: (1) that feedback of nutrients from degrading benthic deposits of biomass may be reused or recycled to support additional BOD removal; and (2) that certain treatment system characteristics (particularly

ASB System Configurations	Theoretical Explanation	Selected References
Lower initial mixing intensity	Increase volume over which BOD is removed, allowing biomass settling and benthal feedback of nutrients in more biologically active zones.	[24,33]
Step feed of effluent	Introduce untreated wastewater at several locations in the basin near areas of nutrient feedback.	[11,23]
Effluent recirculation	Return a portion of treated effluent rich in nutrients sourced from biomass degradation in settling zones near ASB outlet.	[23,33]
Promoting N fixation	Fixation of atmospheric N can occur in some systems; management of ammonia and possibly dissolved oxygen are necessary to maximize growth of N fixers.	[11,17,34]

I. Design and operational factors favoring low-nutrient effluents at aerated stabilization basins (BOD = biological oxygen demand; N = nitrogen).

low ammonia concentrations from purposeful lack of supplementation with the nutrient) can promote fixation of atmospheric N as a nutrient source.

Historically, many ASBs have been configured such that the majority of aeration horsepower is applied near the point where wastewater enters the basin, where BOD demand is highest, with a tapering of aeration or mixing in the mid and latter portions of the system to allow for settling of biomass generated earlier in the basin. Nutrient yields from these benthic deposits of biomass can be significant, and several system configurations have been conceived with the idea that these nutrients might be reused or recycled to support treatment of BOD. While a detailed description of each is beyond the scope of this article, **Table I** describes some of these configurations, theoretical explanations for promoting nutrient reuse, and references where more information is available. The viability of adopting any of the design and operational factors shown in the table at an existing site depends on a number of factors related to the physical layout of the ASB.

Minimizing particulate forms of nutrients

Whether from AS or ASB systems, it has become increasingly common for regulatory agencies to establish treated effluent targets for nutrients as TP or TN, and because a portion of effluent suspended material is residual biomass containing N and P within the cell structure, management of total suspended solids (TSS) in treated effluents can be an important aspect of nutrient minimization. As noted earlier, bacterial composition with regard to nutrients varies, as does the proportion of biomass in effluent suspended solids. Nonetheless, TN and TP contributed by residual biomass can be significant and effluents with lower concentrations of TSS tend to have lower levels of TN and TP. For example, at assumed biomass N and P contents of 10% and 2%, respectively, every 10 mg/L of TSS that is biomass in a treated effluent would contribute 1 mg/L of N and 0.2 mg/L of P to the effluent.

SYMPTOMS OF AND MONITORING FOR NUTRIENT DEFICIENCY

Nutrients are a prerequisite for effective biological treatment of wastewater. While minimizing use of supplemental nutrients is mandated for both economic and environmental protection reasons, overly aggressive efforts can lead to nutrient deficient conditions and corresponding upsets in wastewater treatment plant performance. The most common characteristics of nutrient deficiency are elevated effluent soluble BOD; changes in the observed physical properties of biomass such as increased numbers of filamentous organisms either within or extending from the biological floc; changes in settling rate or compaction (as measured by underflow concentration, sludge volume index, or some other means) in secondary clarifiers; or changes in effluent TSS concentrations. Of course, changes in biomass properties and BOD treatment efficiency can occur for reasons other than nutrient deficiency (e.g., toxicity, sludge age), and thus part of the value of a mature nutrient monitoring program can be to rule out nutrient deficiency as a cause for a change in biomass properties.

Nutrient deficiency in ASB systems can be more complex to diagnose because biomass is not commonly observed as an operational variable as it is in AS systems. Thus, a frequent first indication of inadequate nutrients in ASBs is increased effluent soluble BOD_5, but this is a delayed indicator owing to basin hydraulic retention time and the duration of the BOD_5 test itself. Further, increased soluble BOD_5 may be attributable to system stresses other than nutrient levels, such as increased loading, reduced retention time (i.e., higher flows), extreme temperatures (high or low), or toxic inhibition of the biomass.

In situations where mills have become aware that their treatment systems may be particularly sensitive to upsets caused or exacerbated by nutrient deficient conditions, many have sought to augment system monitoring practices with measurements of biomass condition linked to nutrient availability. Some of these methods are listed in **Table II**, along with theoretical explanations for their links to biomass char-

Measurement	Theoretical Explanation	Selected References
Soluble BOD measurement	A direct measure of residual, degradable BOD in wastewater, thus an indicator of treatment system BOD removal efficiency.	
%N and %P in MLVSS	Semi-quantitative[1] measurement of N and P in biomass.	[9,35]
Extracellular polymer (EPS)	Extracellular polymer content and charge of bacteria can change under nutrient deficient conditions.	[21,36,37,38,39]
Microscopic examination of biomass	Visual and semi-quantitative observation of floc structure and relative abundance of filamentous organisms.	[21]
[1]Results are semi-quantitative because composition of MLVSS may include non-biomass volatile solids (e.g., fiber) that bias results, particularly in samples with lower concentrations of biomass such as those in some ASBs.		

II. Measurements that may correlate biomass performance with nutrient conditions (BOD = biological oxygen demand; MLVSS = mixed liquor volatile suspended solids; N = nitrogen; P = phosphorus).

acteristics and thus treatment system operational stability. As is the case when establishing nutrient residual targets, correlations of these measurements to biomass characteristics are system specific and thus the utility of these measurements should be demonstrated over time under both normal and abnormal conditions prior to relying on them for operational control.

SUMMARY

It is expected that mill environmental managers will continue efforts to optimize supplemental nutrient addition at wastewater treatment plants as a means to minimize costs and release of N and P in treated effluents. Effective secondary biological treatment of wastewater requires availability of nutrients, and thus there is tension between the goals of effective biological treatment and limiting supplemental nutrient use and associated residual loads in treated effluents. Short of expending significant capital for tertiary treatment to remove residual nutrients [25], strategies for improving mill-specific relationships between nutrient requirements and effective biological treatment offer the best opportunities for optimizing nutrients through the use of process control.

Efforts to optimize supplemental nutrient addition and residual nutrients in treated effluents is, particularly for AS systems, best accomplished through strategic and frequent monitoring of the wastewater treatment processes for nutrient levels in, or that correlate to, residuals in biologically active areas of the treatment system. Alternatives to conventional configurations of ASB systems can offer opportunities for reducing or eliminating the need for supplemental nutrient addition by optimizing reuse or recycling of nutrients derived from biomass decay or, for N, encouraging growth of N fixing bacteria. Monitoring location, frequency, and use of measurements that may correlate nutrient availability with biomass characteristics are system specific. Thus, effective nutrient optimization programs necessarily evolve over time as the understanding of relationships between operational monitoring data and treatment plant performance becomes more mature. **TJ**

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Mills operating their own wastewater treatment plants are aggressively pursuing options for minimizing nutrient levels in treated final effluents. The drivers for such actions are usually related to cost conservation and reducing environmental impact.

While this work is introductory and meant to be broadly useful, our challenge was to consider nutrient needs and management practices generally, while mill solutions are often quite site-specific. Mills interested in investigating ways to further optimize nutrient addition may find the information in this article of value.

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