

## **Best Management Practices Guide for Nutrient Management in Effluent Treatment**

**April 25, 2008**

## Foreword:

This report was produced by Rick Marshall, Marshall Environmental Training and Consulting (METC) Group under contract to the Forest Products Association of Canada.

Special thanks to FPAC Member Companies that participated on the FPAC BMP Steering Committee and to NCASI and FP Innovations - PAPRICAN for their participation in the Steering Committee and for their expert guidance throughout the project.

Thanks also to Greg Kaminski and others at Environment Canada for their participation in the peer review process.

## Table of Contents

1.0 Background.....	5
2.0 Purpose.....	6
3.0 Nutrients.....	6
3.1 Forms of nitrogen and phosphorus present in wastewater treatment.....	6
3.1.1 Nitrogen .....	7
3.1.2 Phosphorus.....	7
3.2 Need for Nitrogen and Phosphorus in Biological Treatment Systems .....	8
3.2.1 Activated Sludge	
3.2.2 Pure Oxygen Activated Sludge	
3.2.3 Aerated Stabilization Basins (ASBs)	
3.3 Sources of Nitrogen and Phosphorus.....	10
3.3.1 Kraft Mills.....	10
3.3.2 Recycle Mills .....	11
3.3.3 Mill Additives .....	11
3.3.4 Supplements.....	11
3.3.5 Biological release.....	12
3.3.6 Shock Loads.....	12
3.3.7 Side streams .....	12
3.3.8 Boiler Ash .....	13
4.0 Managing Nutrients .....	13
4.1 Sampling .....	13
4.1.1 Activated Sludge.....	13
4.1.2 ASBs .....	13
4.2 Analyses.....	14
4.2.1 Nitrogen Analyses.....	15
4.2.2 Phosphorus Analyses .....	15
4.2.3 On-line Analyzers .....	15
4.3 Feed Equipment .....	15
5.0 Strategies to Control N and P.....	16
5.1 Control to Residual Targets .....	16
5.2 Control to BOD:N:P ratio .....	17

5.3 Control to Influent Organic Loading Measurement.....	17
5.3.1 BOD .....	18
5.3.2 COD .....	18
5.3.3 TOC.....	19
5.3.4 Pure Oxygen Reactor Oxygen Flow .....	19
5.4 Control to On-line Continuous Residual Measurement.....	20
5.5 Control to Influent Flow .....	21
5.5.1 Control to Influent Flow Adjusted by COD/TOC Input.....	22
5.6 Control to Production.....	22
5.6.1 Control to Grade Type .....	23
5.7 Control of ASB Nutrients.....	23
6.0 Minimizing Nitrogen and Phosphorus Discharges .....	23
6.1 Control Effluent TSS .....	24
6.1.1 Activated Sludge.....	24
6.1.2 ASBs .....	24
6.2 Properly Manage Supplement Feed Rates .....	25
6.3 Change Mill Operations – Use Different Chemicals, Modify Production Processes	
6.4 Mill Shutdown Impacts.....	25
6.5 Revise Treatment Plant Operation .....	26
6.5.1 Equalization or Spill Basins.....	26
6.5.2 Reroute Side Streams.....	27
6.5.3 Secondary Clarifiers.....	27
6.6 Physical Treatment Plant Changes.....	27
6.6.1 Activated Sludge.....	27
6.6.2 ASBs .....	27
6.7 Incorporate Nutrient Removal Processes If Needed.....	28
7.0 Implementation .....	29
7.1 Operator training.....	29
7.2 Developing an Operating Plan and Targets .....	29
7.2.1 Managing Nitrogen and Phosphorus Decision Keys .....	29
7.3 Fine-tuning.....	35
Appendix.....	36
References.....	40

# 1.0 Background

The Canadian Environmental Effects Monitoring (EEM) program has shown that there is enrichment in some receiving waters downstream from pulp and paper mills. This is based on the national assessment of the Cycle 1 to Cycle 3 data involving both fish and benthic invertebrates <sup>[2]</sup>. In the case of fish, the national response pattern for effluent exposed species is larger liver, faster growth rate and larger condition factor. In the case of benthic invertebrates, the national response pattern for effluent exposed organisms include increased abundance with some combination of increases, decreases or no change in taxon richness. The origin and type of enrichment are not known in all cases, but nitrogen and phosphorus are suspected.

Nitrogen and phosphorus come from both point source and non-point source discharges to aquatic environments. Reducing nitrogen and phosphorus in discharges can be partially accomplished through controlling point source discharges, which are inherently easier to control. Non-point source discharges, such as storm water runoff from agricultural and urban areas, are much more difficult to control.

There are a number of receiving water problems that can be caused by excessive nitrogen and phosphorus. Nitrogen can cause problems in receiving waters such as aquatic toxicity (ammonia), oxygen depletion (conversion of ammonia to nitrate), and excessive algae and plant growth commonly referred to as eutrophication. Phosphorus can also lead to eutrophication. Eutrophication can lead to diurnal oxygen depletion because of the photosynthesis cycle. It also can lead to taste and odour problems caused by the decay of the algae and aquatic plants. Note that only the soluble forms of nitrogen and phosphorus can lead to eutrophication. <sup>[8]</sup> Nitrogen and phosphorus contained in solids cannot lead to eutrophication unless the solids are somehow broken down or degraded thus releasing soluble nitrogen or phosphorus into the aquatic environment.

Some mills discharging to sensitive streams and rivers already have nitrogen and phosphorous limits in their discharge permits. Many other mills that do not currently have nitrogen and phosphorus limits in their permits are now being asked to monitor the nitrogen and phosphorus in their discharge. In the latter case, regulating agencies may collect nitrogen and phosphorus information to help determine the potential impacts on the receiving watershed and whether nitrogen and phosphorus limits are needed to reduce the impacts these nutrients are having on the receiving watershed.

So what are the benefits in minimizing nitrogen and phosphorus in final discharges? Depending on the receiving waters, the benefits are improved stream health and fish habitat, improved aesthetics, reduced algal blooms and good quality drinking water supplies, along with the benefit of cost savings resulting from a reduced need to supplement purchased nitrogen and phosphorus.

The challenge for mills addressing nutrient management is to maintain a sufficient degree of effluent treatment while at the same time minimizing nutrient residuals. If nutrient levels get too low, treatment efficiency drops resulting in higher effluent TSS and BOD. Interestingly, however, this can also temporarily result in higher nitrogen and phosphorus residuals because of the nitrogen and phosphorus contained in the biological solids being lost to the final effluent.

## 2.0 Purpose

The purpose of this guide is to help mills develop a site-specific Best Management Practices (BMP) plan for nutrient management. This guide includes examples and example decision keys illustrating important points about managing nutrients applicable to activated sludge treatment systems and aerated stabilization basins. In Canada, approximately two-thirds of the biological treatment systems are activated sludge systems of various designs, while about one-third are aerated stabilization basins, which are mainly located at kraft mills. The breakdown is shown in the following table.

Activated sludge:	70
– Conventional:	48
– Oxygen (OAS):	12
– SBR:	10
Aerated stabilization basin (ASB):	34
Anaerobic (UASB or IC):	2
Attached growth (Acticontact, Anoxkaldnes):	3

Mills should select from the information presented relative to their specific mill characteristics, along with their type of treatment system, in order to develop a customized BMP that is site-specific for the mill.

The guide is intended to be as practical as possible and focuses on the treatment system itself. Mention is made of the importance of process control, but the specifics of this are considered outside of the scope of this Guide. Each mill must make its own efforts to review BOD loadings to the treatment system recognizing the important link between mill wastewater treatment plant performance and nutrient requirements. There is a balance between ensuring treatment systems do their job (meeting toxicity and BOD/TSS regulatory limits) and minimizing impacts associated with excess nutrient discharges.

## 3.0 Nutrients

### ***3.1 Forms of nitrogen and phosphorus present in wastewater treatment***

Nitrogen and phosphorus can exist in a variety of forms in mill wastewater. It is important to understand: 1) what these forms are; 2) which forms of nutrients the treatment system bacteria use; and 3) which forms can pass through the treatment system

unused by the bacteria. Knowing which nutrient forms are present in the final effluent allows mills to better identify the probable cause(s).

### 3.1.1 Nitrogen

Nitrogen can be present in the following forms: organic nitrogen, ammonia, nitrite and nitrate. Total nitrogen is determined from the sum of all four forms. <sup>[1]</sup>

Ammonia is the key nitrogen form that is used by bacteria for BOD oxidation. The bacteria start working immediately when they come in contact with BOD so it is very important that ammonia is present at the beginning of biological treatment.

Organic nitrogen must be converted into ammonia first before it can be used as a nutrient. During this conversion, the bacteria function nitrogen deficient unless there is some ammonia present.

Depending on the complexity of the organic nitrogen, some of it may not be available as a nutrient as it takes time for the bacteria to convert it into ammonia. In the activated sludge treatment systems with hydraulic detention times in hours, there probably is not enough time for the bacteria to convert all organic nitrogen into ammonia. With more treatment time available in larger systems such as ASBs (aerated stabilization basins) and in activated sludge systems with multiple day detention times, bacteria can convert the organic nitrogen to ammonia and use it as a nutrient.

Ammonia exists either as ammonium ion ( $\text{NH}_4^+$ ) or as ammonia ( $\text{NH}_3\text{-N}$ ) depending on the pH. As the pH rises above 7, ammonia exists as  $\text{NH}_3\text{-N}$  (un-ionized), which becomes toxic to fish in low concentrations at pH over 8 (see Appendix). If the pH is below 7, ammonia exists more as ammonium ion ( $\text{NH}_4^+$ ), which is much less toxic.

Nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ) are nitrogen forms usually found in aerobic treatment systems because of adding excess nitrogen. This process is called nitrification where ammonia is converted through nitrite to nitrate by the more commonly known nitrifying organisms, *Nitrosomonas* and *Nitrobacter*. Nitrification is an aerobic process so it would occur in the aerated basins. Unless nitrite and nitrate are being added to the treatment system, they should not be present in appreciable amounts if the nitrogen feed rate is being managed properly. These forms will disappear if denitrification occurs as the bacteria switch from aerobic respiration to nitrate respiration if some BOD is present and dissolved oxygen (D.O.) levels are low. The end product is nitrogen gas, which releases to the atmosphere. Denitrification would occur in low to no D.O. conditions such as in secondary clarifiers or ASB quiescent zones.

Nitrogen fixation has been reported at a few mill ASB treatment systems. <sup>[11]</sup> This process is activated under low nitrogen and oxygen conditions by bacteria that have a specific enzyme system to fix nitrogen. Most mill treatment systems do not have nitrogen fixation as a source of nitrogen.

### 3.1.2 Phosphorus

Phosphorus exists in the following forms: orthophosphate, polyphosphate and organic phosphate. Total phosphorus equals the sum of all three forms.

The bacteria readily use orthophosphate ( $\text{PO}_4^{-3}$ ) for BOD oxidation. Polyphosphate must be hydrolyzed into orthophosphate and this takes some time. Organic phosphate must also be converted into orthophosphate and this takes even longer. If orthophosphate is not

present when the bacteria come in contact with BOD, they will function phosphorus deficient.

### **3.2 Need for Nitrogen and Phosphorus in Biological Treatment Systems**

Bacteria use nitrogen (ammonia) and phosphorus (orthophosphate) to metabolize organic carbon molecules (BOD) into new cells, carbon dioxide and water. To do this, they use the nitrogen and phosphorus to manufacture enzymes. Enzymes are the tools bacteria then use to break down the organic carbon molecules. Each type of organic molecule can be broken apart by a specific enzyme(s). Because most wastewaters contain many different types of organics, numerous types of bacteria that produce different enzymes are needed in order to breakdown the different types of organics.

If the bacteria are deficient in nitrogen or phosphorus, settling problems and foaming problems can occur. Certain types of filamentous bacteria can outgrow floc-forming bacteria that are functioning under nitrogen or phosphorus limiting conditions causing settling problems. Bacteria can produce excess polysaccharide under nutrient limiting conditions resulting in foaming, settling and dewatering problems. <sup>[4]</sup>

Final effluents can become toxic if the bacteria lack the proper amount of nitrogen and phosphorus. Being slightly deficient in nutrients can prevent the bacteria from breaking down the complex toxic organic molecules into simpler molecules. This means these complex toxic molecules can pass through untreated into the final effluent. It is very important that the proper amounts of ammonia and orthophosphate are present to achieve proper BOD removal and prevent toxicity in the final effluent.

The following are discussions of the nutrient ratios for different biological processes – activated sludge, pure oxygen activated sludge and aerated stabilization basins.

**3.2.1 Activated Sludge.** The theoretical nutrient requirements in activated sludge treatment systems are for every 100 kgs of BOD, the bacteria require 5 kg of nitrogen and 1 kg of phosphorus. This is commonly referred to as the BOD:N:P ratio of 100:5:1. In actual operation, the ratio will probably be lower such as 100:4.5-4.8:0.5-0.8. <sup>[3]</sup> The actual ratio is site specific and needs to be determined through actual operation. The 100:5:1 ratio is a good starting point for systems to determine their site-specific ratio.

To calculate the BOD:N:P ratio, you need the following data: secondary BOD loading in kg/day, the amount of nitrogen added in kg/day and the amount of phosphorus added in kg/day. If the wastewater entering the biological treatment unit contains nitrogen and phosphorus, these amounts need to be included in the calculation.

#### **Example calculation of the BOD:N:P ratio.**

BOD loading –	20,500 kg/day
Ammonia Feed (18% sol'n, Specific Gravity 0.93) -	4,530 L/day
TKN loading from wastewater -	323 kg/day
Pho. Acid Feed (55% sol'n, Specific Gravity 1.52) -	610 L/day
Phosphorus Loading from wastewater -	53 kg/day

#### **1) Calculate kg of N per L of ammonia feed solution.**

NH<sub>3</sub> is 82% N (Molecular Weights - N = 14, H = 1)

$$\begin{aligned} \text{N, kg/L} &= .82 \times .18 \times .93 \\ &= .137 \text{ kg N/L} \end{aligned}$$

**2) Calculate kg of N.**

$$\begin{aligned} \text{N, kg/day from feed} &= .137 \text{ kg/L} \times 4,530 \text{ L/day} \\ &= 622 \text{ kg/day} \end{aligned}$$

$$\begin{aligned} \text{Total N, kg/day} &= \text{ammonia fed} + \text{wastewater TKN} \\ &= 622 \text{ kg} + 323 \text{ kg} \\ &= 945 \text{ kg N/day} \end{aligned}$$

**3) Calculate BOD:N ratio.**

$$\begin{aligned} \text{N} &= (100 \times \text{kg N}) / \text{kg BOD} \\ &= (100 \times 945) / 20500 \\ &= 4.6 \end{aligned}$$

$$\text{BOD:N Ratio} = 100:4.6$$

**4) Calculate kg of P per L of phosphoric acid feed solution.**

H<sub>3</sub>PO<sub>4</sub> is 32% P (Molecular Weights – H = 1, P = 31, O = 16)

$$\begin{aligned} \text{P, kg/L} &= .32 \times .55 \times 1.52 \\ &= .268 \text{ kg P/L} \end{aligned}$$

**5) Calculate kg of P.**

$$\begin{aligned} \text{P, kg/day from feed} &= .268 \text{ kg/L} \times 610 \text{ L/day} \\ &= 163 \text{ kg/day} \end{aligned}$$

$$\begin{aligned} \text{Total P, kg/day} &= \text{phosphorus fed} + \text{wastewater phosphorus} \\ &= 163 \text{ kg} + 53 \text{ kg} \\ &= 216 \text{ kg/day} \end{aligned}$$

**6) Calculate BOD:P ratio.**

$$\begin{aligned} \text{P} &= (100 \times \text{kg P}) / \text{kg BOD} \\ &= (100 \times 216) / 20,500 \\ &= 1.05 \end{aligned}$$

$$\text{BOD:P ratio} = 100:1.05$$

$$\text{BOD:N:P ratio} = 100:4.6:1.05$$

Be aware that nitrogen and phosphorus requirements could vary between summer and winter. In cooler temperatures, sludge yields are higher with the bacteria utilizing more nutrients for cell growth. In warmer temperatures, sludge yields are lower and the bacteria utilize less nutrients. If the aeration basin temperatures vary between summer and winter, the nutrient requirements will change, which means the BOD:N:P ratio will differ between summer and winter. Developing a correlation between nutrient requirements and basin temperature will help the operators make seasonal adjustments to the BOD:N:P ratio.

Conventional air activated sludge systems can operate at lower BOD:N:P ratios depending on the loading and detention time of the aeration basin. Systems with the longer detention times typically operate at lower ratios because of the lower organic loadings and some recycling from bacterial cell decay called endogenous respiration. Systems with shorter detention times need to operate closer to the 100:5:1 ratio because of high loadings and little recycling of nutrients from cell decay.

**3.2.2 Pure Oxygen Activated Sludge.** These systems (UNOX, OASES) are considered high rate systems where higher BOD loadings are applied to the reactors that operate at much shorter detention times than for conventional aerated systems. Biological activity is much faster as the bacteria function in an oxygen rich environment created in a covered, slightly pressurized biological reactor. Because of this, these systems tend to operate closer to the BOD:N:P ratio of 100:5:1.

**3.2.3 Aerated Stabilization Basins (ASBs).** Aerated stabilization basins operate at lower BOD:N:P ratios than activated sludge systems. Reasons for this include the release of nutrients from endogenous decay in aerated zones because of low organic loading and from the release of nutrients from anaerobic breakdown of settled sludge (benthic layer). This is referred to as benthic feedback. However, if the benthic feedback occurs after BOD oxidation then it is not available as a nutrient. This means this ASB has to operate at slightly higher BOD:N:P ratios than the ASB that allows benthic decay from the sludge layer under the aerated zone. A typical ratio for an ASB system is 100:2.5-3.0:0.5-0.8. <sup>[4]</sup>

Note that if benthic feedback occurs, it raises the potential for ammonia toxicity to occur in the final effluent and failure of the regulated fish toxicity test.

### ***3.3 Sources of Nitrogen and Phosphorus***

Nitrogen and phosphorus are present in virtually all mill wastewaters. The amount and type of nitrogen and phosphorus present in the mill wastewater depends on the type of mill, grades of products manufactured and the chemicals used in the mill. It also depends on the type of wood used and source of recycled fiber.

Some of the nitrogen and phosphorus in the wastewater will be used as a nutrient because it is present in, or can be converted to, a usable form such as ammonia. Some of the nitrogen and phosphorus present in the mill effluent will pass through in the final effluent because it is present in an unavailable form.

Because most mill wastewaters are deficient in the amount of nitrogen and/or phosphorus required for bacterial metabolism, nutrient supplements must be added to achieve proper biological treatment. The amount added depends on the available nutrients in the wastewater and other sources, the organic loading to the biological treatment unit and the amount released from microbial decay.

#### **3.3.1 Kraft Mills**

Nitrogen sources in kraft mills <sup>[9]</sup> are from lignin, black liquor and fowl condensates. The nitrogen content in lignin, which is organic nitrogen, varies depending on the type of wood. This residual lignin generally is not completely available as a nitrogen nutrient because it is too complex. Some of it may be broken down biologically to ammonia in the treatment system possibly making it available as a nutrient. The nitrogen in black liquor would be similar in that some of it maybe converted into ammonia.

Foul condensates contain a significant amount of ammonia. If the foul condensates are hard piped to the biological treatment process and not stripped out, this ammonia will be available as a nutrient.

Lime mud will probably contain some phosphorus depending in the purchase lime make-up to the recausticizing system.

### **3.3.2 Recycle Mills**

Depending on the recycle fiber, recycle mill wastewaters can contain significant amounts of nitrogen and phosphorus. This makeup will change depending on the fiber sources used. Starches, especially potato starch, are high in nitrogen. <sup>[5]</sup> Recycling of laundry soap containers could contain high amounts of phosphorus. It is probably best to measure the nitrogen and phosphorus in the wastewater under different mill operating conditions (type of fiber, type of pulp or paper grade being produced) and develop a database on what levels of nitrogen and phosphorus can be expected in the wastewater during different operations.

### **3.3.3 Mill Additives**

There are numerous chemicals used in mill operations that contain nitrogen and/or phosphorus. These chemicals include <sup>[9]</sup>:

- Defoamers (nitrogen or phosphorus)
- Water conditioners (nitrogen and/or phosphorus)
- Scale inhibitors (nitrogen and/or phosphorus)
- Chelants (nitrogen and/or phosphorus)
- Biocides and slimicides (nitrogen)
- Wet and dry strength additives (nitrogen)
- Dyes and pigments (nitrogen)

Mills need to work with their chemical supplier and identify the chemicals that contain nitrogen and phosphorus. In mills where the chemicals used in the mill exceeded the nutrient requirements for secondary treatment or passed through the treatment system unused, the suppliers had to find substitutes for these chemicals in order to lower the nitrogen and phosphorus levels in the wastewater.

### **3.3.4 Supplements**

Because most mill effluents are deficient in available nitrogen and phosphorus, nitrogen and phosphorus supplements are added to achieve proper BOD removal in the biological treatment unit.

Nitrogen supplements used include: anhydrous ammonia, aqua ammonia, urea (liquid or dry) and combinations such as ammonium nitrate, UAN (urea-ammonium-nitrate), ammonia sulfate, ammonium phosphate, ammonium polyphosphate, diammonium phosphate.

The main phosphorus supplement is phosphoric acid. Other phosphorus supplements include the nitrogen-phosphorus combinations mentioned above.

Combined nitrogen-phosphorus supplements can be more difficult to control because one chemical is used to meet two requirements. It often ends up in overfeeding or underfeeding one nutrient while meeting the requirement for the other nutrient.

### **3.3.5 Biological Release**

As cells die, they lyse open releasing nitrogen and phosphorus into the water. This is called endogenous decay. This occurs in aeration basins with long hydraulic detention times and in secondary clarifiers with long sludge detention times. This is magnified during mill shutdowns when there is not enough food present for the bacteria to sustain themselves.

Biological release also occurs in ASBs. It can occur from aerobic endogenous decay in the water. It also occurs from anaerobic decay in benthic sludge layers.

### **3.3.6 Shock Loads**

Shock loads are sudden increases in the amount of material entering the treatment system. Shock loads are usually associated with spills but they can also be associated with certain mill procedures that result in higher sewer losses. Backwashing of demineralizers, for example, is an example of a routine procedure that can cause a shock load. The issue of shock loads applies particularly to kraft and sulphite mills that carry inventories of organic material (black liquor, etc.) where even small liquor losses to sewer can have an impact on the organic loads to the treatment system. Many mills have spill containment and based on mill specific criteria divert effluent to the spill thereby reducing the magnitude of the shock loads.

Shock loads also occur at other types of mills since they have chemical tanks and oil tanks that can be a source of sudden discharges to the sewer. Most mills have biocides on site and these could be a source of shock loads.

Shock loads will impact the bacteria especially if they are inhibitory or toxic. If the shock load is inhibitory, the bacteria will not utilize all of the nutrients present since they are not processing the entire BOD entering the system. If the shock load is toxic, the bacteria will die off releasing nutrients into the water. Oxygen respiration rates and D.O. residuals will help confirm if a shock load has entered the system. Respiration rates will drop and D.O. residuals will increase during shock load events.

### **3.3.7 Side Streams**

Sludge dewatering pressates and filtrates are a side stream containing nitrogen and phosphorus because they are released during the processing of biological solids. The amount present depends on the conditioning and dewatering processes used (belt press, screw press, screw press with steam, acidification).

Landfill leachate may contain nitrogen and phosphorus especially if dewatered sludge and boiler ash is sent to the landfill. Sludge decomposes over time releasing nutrients and BOD that will end up in the leachate.

Some mills are using sludge acidification as a way to condition their sludge and promote more water release prior to dewatering. Acidifying the sludge will release more nutrients into the water, which eventually gets returned to the treatment system.

Care must be taken to ensure that the side streams returned to the treatment system do not lead to errors in calculating nutrient balances.

### **3.3.8 Boiler Ash**

Boiler ash has been found to contain phosphorus, which means that the ash handling system can be a source of nutrient. Instead of directly sending ash to landfill, some mills sewer the boiler ash to the primary clarifier where the phosphorus is dissolved in the effluent ahead of secondary treatment.

## **4.0 Managing Nutrients**

For proper nutrient addition management, mills need to select correct sampling locations, handle samples properly so that the nutrient residuals do not change prior to analysis, conduct proper analytical testing for the different forms of nutrients and have proper nutrient feeding equipment. Inaccurate residual measurement is one of the main reasons that nutrient feeds are difficult to control.

Because biological samples contain microorganisms, nutrient residuals will change over time. It is best to filter these samples immediately after collection so that the true nutrient residual can be measured. The other option is to refrigerate the samples to slow down biological activity but it takes time to cool down samples from warm basins. Filtering samples is preferred. Most mills use their standard TSS filter paper for filtering. A few mills are using a disposable sterile plastic filtering unit in the field that produces filtrates with no bacterial cells whereas the standard filter paper may allow some bacteria to pass through depending on the pore size.

### **4.1 Sampling**

The key parts of a sampling program are having correct sampling location(s) and proper handling of the samples so that the nutrient residuals do not change before they are tested. Sampling location is site specific and depends on the type of treatment system and its physical layout.

#### **4.1.1 Activated Sludge**

In activated sludge systems, nutrient residual samples are usually taken from the effluent end of the aeration basin because this is assumed to be where BOD oxidation is complete. However, in aeration basins with long detention times, the residuals will probably differ between where BOD oxidation is completed and the aeration basin effluent because of nutrient release from endogenous decay.

Utilizing residuals from the secondary clarifier effluent will probably not be useful for process control because the residuals will change if biological activity occurs in the clarifiers. Nitrates will decrease as D.O. levels decrease due to nitrate respiration (denitrification). Residuals will change if the sludge undergoes further anaerobic respiration because of long sludge detention times.

So for achieving quality BOD removal, the residuals at the end of treatment in the aeration basin are the important ones to measure and target for. The residuals at the end of large aeration basin effluents can give a false high for biological treatment needs. However, these residuals represent the more probable final effluent nutrient residuals.

#### **4.1.2 ASBs**

In ASB systems, nutrient residual samples should be taken in a couple of locations. The first location would be at the end of aerobic treatment zone to ensure that proper nutrient

requirements were met for BOD oxidation. The second location would be at the end of the quiescent zone because of the release of nutrients from anaerobic decay of the settled solids.

## 4.2 Analyses

The methods used to test for nitrogen and phosphorus differ depending on the desired parameter.<sup>[8]</sup> Most of the methods measure an inorganic form of nitrogen or phosphorus. The inorganic forms of nitrogen are ammonia, nitrite or nitrate. The major inorganic form of phosphorus is orthophosphate. There are also other insoluble forms of inorganic phosphate, which also have to be considered (calcium, iron and aluminum phosphate maybe present in the sample as inorganic precipitates).

For the organic forms, the methods usually involve a digestion step to convert the organic form to an inorganic form first and then it is measured as an inorganic. These samples are not filtered so that the nitrogen and phosphorus contributions from solids are measured along with the soluble concentrations.

To determine Total Nitrogen and Total Phosphorus, more than one test is used for both. Total nitrogen is the sum of organic nitrogen plus the inorganic forms – ammonia, nitrite and nitrate. Total phosphorus is the sum of orthophosphate plus organic phosphate and polyphosphate.

### **Forms of Nitrogen:**

$$\text{Total Nitrogen (TN)} = \text{Organic Nitrogen} + \text{Total Inorganic Nitrogen (TIN)}$$

$$\text{Organic Nitrogen} = \text{TKN (Total Kjeldahl Nitrogen)} - \text{Ammonia (NH}_3\text{)}$$

$$\text{Total Inorganic Nitrogen (TIN)} = \text{Ammonia (NH}_3\text{)} + \text{Nitrite (NO}_2^-) + \text{Nitrate (NO}_3^-)$$

### **Forms of Phosphorus:**

$$\text{Total Phosphorus (TP)} = \text{Orthophosphate (PO}_4^-) + \text{Polyphosphates} + \text{Organic P}$$

Many of the test methods are colorimetric. With pulp and paper wastewaters that have color, it becomes more difficult to detect nutrient residuals using colorimetric methods. The colorimetric nitrogen methods that have a yellow endpoint are more difficult to detect. Orthophosphate colorimetric tests have a blue end point making it a bit easier to detect.

Other analytical methods involve ion selective probes (ammonia, nitrate) and ion chromatography (ammonia, nitrite, nitrate, orthophosphate). The ion selective probes require calibration using prepared standards. Standards must be stored in the dark and be prepared fresh for the lower concentrations for proper calibration. If the concentrations of the standards are not close to the concentrations of the wastewater samples, then the probe calibration will be off leading to inaccurate measurement of the residuals.

Ion chromatography is a more expensive method because of instrument cost but is being used because it provides accurate residuals for different forms of nitrogen and phosphorus. With accurate residuals, mills can tighten up on their nutrient management achieving cost savings with lower nutrient feed rates to offset the cost of the instrument.

Provided in the appendix is a list of analyses for measuring the different forms of nitrogen and phosphorus and their potential interferences.

#### 4.2.1 Nitrogen Analyses

**Ammonia.** This can be measured using colorimetry, ion selective probes and ion chromatography. Colorimetric procedures are affected by turbidity and color so samples are filtered first before testing. Ammonia ion probes can be used to measure ammonia but they require standardization using a series of prepared standards (100 mg/L, 10 mg/L, 1 mg/L and 0.1 mg/L). It is important to use standards around the expected residual. Calibrating with only higher concentration standards will not provide for accurate measurement at the lower concentrations.

**Nitrite/Nitrate.** These can be measured colorimetrically. There is a nitrate ion probe that can be used but it detects other ions as well. These must be suppressed using a chemical suppressor so that only nitrate is measured. Ion chromatography is also used to measure these residuals.

**Total Inorganic Nitrogen. (TIN).** There is a colorimetric test that measures the combination of all three inorganic nitrogen species. This end point has a green color making it a little easier to detect instead of the pale yellow color. Nitrite and nitrate are converted chemically back to ammonia first before being measured as ammonia.

**Total Organic Nitrogen.** Total Kjeldahl Nitrogen (TKN) is used to help determine organic nitrogen. TKN test is a digestion test that measures the combination of organic nitrogen and ammonia. To determine the amount of organic nitrogen, the ammonia concentration is subtracted from the TKN concentration.

**Total Nitrogen.** The common method to determine total nitrogen is by combining the TKN and nitrite/nitrate concentrations determined by their respective analysis.

#### 4.2.2 Phosphorus Analyses

**Orthophosphate.** Orthophosphate can be determined colorimetrically and by ion chromatography. The colorimetric end point is a blue color making it much easier to determine in a colored effluent.

**Total Phosphorus.** This requires a digestion step to convert the organic, insoluble inorganic and polyphosphate forms into a soluble inorganic form – orthophosphate. Then the sample is analyzed for orthophosphate.

#### 4.2.3 On-line Analyzers

On-line nutrient analyzers have become much improved since they were first introduced. Problems with the older nutrient analyzers included accuracy, reliability, frequent cleaning and calibration was needed, and frequent replenishing of reagents.

The newer on-line analyzers require less attention because some provide automatic cleaning and calibration. With improved accuracy and less maintenance, these analyzers are becoming more attractive. Since there are numerous suppliers of analyzers, proven track record of reliable operation and minimal maintenance needs over a long period of time will be the best recommendation for selecting an analyzer.

### 4.3 Feed Equipment

Nutrient feed equipment must be properly sized to provide desired dosages of nutrients. This means the equipment must have the proper operating range and be capable of dealing with small feed rate adjustments.

Pumps should have variable speed control. Stroke adjustment should be provided if they are diaphragm type positive displacement pumps. Drawdown tubes should be included so that pumping rates can be verified. Pump flow charts with the pump settings versus flow rates should be used for setting feed rates.

Control systems must be sized appropriately to provide reliable flow rates. Control valve actuators must have tight response to provide desired flow rates. Flow meters must be installed properly for the type of meter so that flow rates are accurately measured for the control valves to work properly.

With large nutrient storage tanks, tracking liquid level becomes challenging when trying to detect small level changes on a daily basis. Utilize proper level measurement devices that provide the greatest degree of detecting small changes in tank level. Tracking daily inventory changes versus desired feed rates could be used to confirm proper nutrient feed rates. This can also be used to track BOD:N:P ratios.

## 5.0 Strategies to Control N and P

There are different strategies that can be used to control nitrogen and phosphorus addition rates. Some may have an advantage over others, but that depends on the type and size of the treatment plant. Some pros and cons are offered for each strategy.

### 5.1 Control to Residual Targets

Most effluent treatment systems measure nutrient residuals and control their nutrient feed based on the residuals versus residual control targets. This can be an acceptable control strategy assuming that the proper residuals are measured in the proper location at a proper frequency. The minimum sampling frequency is once a day.

Note that this strategy is a reactive strategy. Operators react by changing nutrient feed rates based on the residual. Operators will lower a feed rate if a residual is high. If a residual is low, operators will increase a feed rate.

For nitrogen, ammonia, nitrite and nitrate residuals should be measured on filtered samples from the aeration basin. Typical targets are 0.5 – 1 mg/L ammonia. Nitrite/Nitrate residuals should be < 1 mg/L to zero levels.

For phosphorus orthophosphate residuals should also be measured on filtered samples from the aeration basin. Typical target is 0.5 – 1 mg/L orthophosphate.

Note that the residual operating targets are site specific and must be verified through actual operation. High rate systems and systems with short detention times tend to operate at 1 mg/L or slightly higher residuals. Systems with longer detention times tend to operate at lower residual targets.

If the residual targets are too low, sludge quality and effluent quality will change. Sludge quality changes include the growth of nutrient deficient filamentous bacteria and the increased production of polysaccharide. Microscopic exams by experienced outside consultants or in-house staff will confirm sludge changes. If filtering times for MLSS samples noticeably increase, this is a clue that a polymeric substance is present (polysaccharide or polymer used for settling/dewatering) and should be further investigated.

Some mills have proven they must operate at nutrient residual targets  $> 1$  mg/L. <sup>[11]</sup> These mills proved through operating at above and below a specific residual target over several cycles that their treatment systems became nutrient deficient below a certain residual. When the system was operated above the residual, nutrient deficiency disappeared and the plant produced an effluent low in BOD and TSS. The nutrient threshold varied from plant to plant and was specifically determined for each treatment plant.

**Pros:** Reduces chances for overfeeding or underfeeding nutrients as it more closely matches the nutrient requirements based on organic loading and aeration basin performance.

**Cons:** Leads to poor nutrient management if residuals are inaccurate. This strategy could lead to nutrient deficiency if residuals are only measured at the end of large multi-day basins and not at the completion of the aerobic treatment, Nutrients could be released because of endogenous decay occurring towards the end of the aeration basin giving false high effluent residuals.

### ***5.2 Control to BOD:N:P ratio***

The rule of thumb that has been used for feeding nutrients is BOD:N:P ratio of 100:5:1. In actual operations, this ratio will vary depending on the type of mill and treatment system. In many mills the ratio for activated sludge could range from 100:4.5-4.8:0.5-0.8. The ratio for ASBs could range from 100:2.5-3.0:0.5-0.8.

Take note that most mills calculate this ratio based on their supplement feed rates. For mills that have significant nitrogen and phosphorus from other sources, the calculated ratios will seem quite low. These low ratios can be used for control knowing that when the other sources are added into the calculations, the ratios will get closer to 100:5:1.

Mills that try to operate to someone else's ratio because it is lower and it works for them will probably get into sludge settling problems and treatment problems. Remember the ratios are site specific and need to be determined for each plant including seasonal adjustments due to changes in temperature.

**Pros:** Matches nutrient feed to the organic loading based on an established BOD:N:P ratio. Should produce nutrient cost savings and minimize possibility of nutrient deficiency.

**Cons:** Mills cannot use this strategy if organic loading is determined by BOD testing because of the 5-day lag time. This strategy could lead to poor nutrient management if good correlations of BOD with COD, TOC or 1-day BOD measurements are not established.

### ***5.3 Control to Influent Organic Loading Measurement***

Most treatment plants are familiar with BOD<sub>5</sub> (biochemical oxygen demand) since it is a permit requirement in most discharge permits. The test is a five-day test measuring biological degradation through oxygen consumption. Compounds that have long degradation times will not show up in this 5-day test but would show up in longer BOD tests such as BOD<sub>20</sub>. For practical operations in managing nutrient feed, the BOD<sub>5</sub> measurement is not practical for day-to-day control because of the 5-day lag time. Some mills use 1-day BOD to get the estimate of the 5-day BOD.

Many mills use other tests such as COD, TOC and 1-day BOD to get an estimate of the influent organic load. By knowing or predicting the influent organic load, nutrient feed rates could be set to maintain the target BOD:N:P ratio set for the particular mill.

For continuous on-line measurement, mills are starting to look at on-line COD and TOC analyzers. Pure oxygen plants are using oxygen flow as a response indicator to the organic loading.

#### **5.3.1 BOD<sub>1</sub>**

Some mills measure the oxygen depletion after 1 day in during the 5-day BOD test. They then develop a ratio between the 1-day BOD to the 5-day BOD to predict what the 5-day BOD will be. Then based on their BOD:N:P ratio, they set their nutrient feed rates.

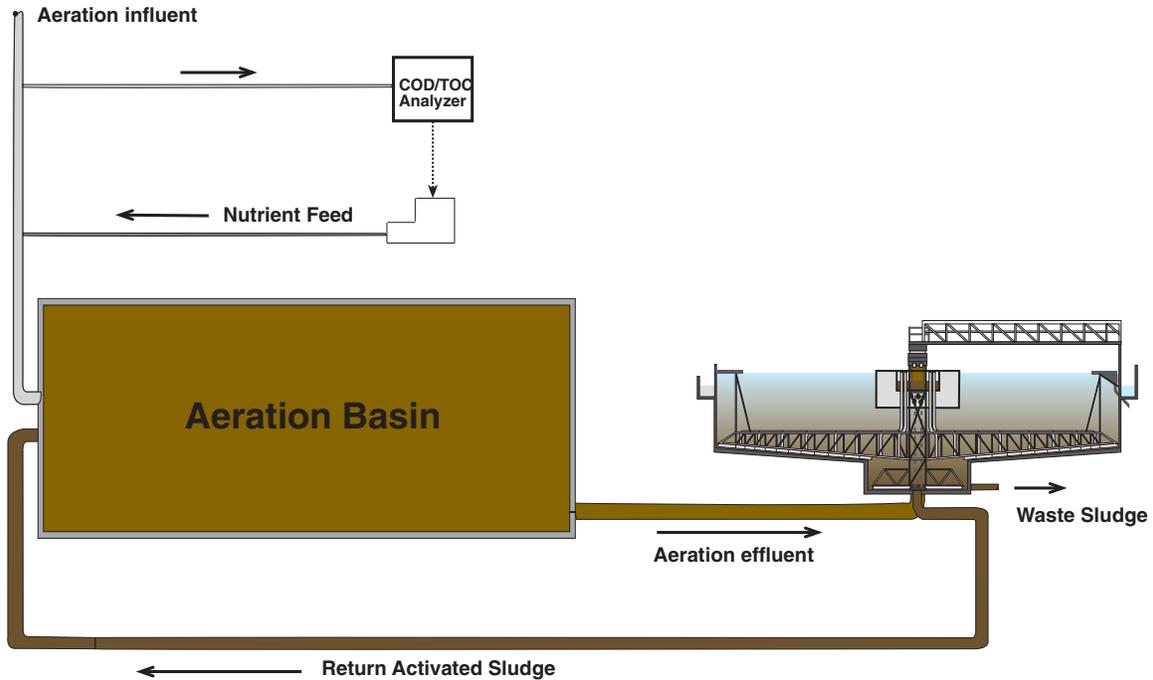
#### **5.3.2 COD**

COD stands for chemical oxygen demand. COD values are higher than BOD values because through the wonders of chemistry a lot more compounds can be oxidized chemically than they are biologically. For most mills, there will be a fraction of non-biodegradable COD that passes through in the final effluent. An effluent low in BOD can have a high effluent COD value.

Kraft mill tends to have higher non-biodegradable CODs. Other mills such as mechanical pulp mills tend to have lower non-biodegradable CODs because most of the influent organics are biodegradable. Recycle mills differ in levels of non-biodegradable CODs because of the type(s) of furnish and the treatment processes.

Many mills try to establish a COD:BOD ratio so they can get an idea of the BOD load instead of waiting for 5 days for BOD results. Some mills have trouble establishing this ratio because of varying solids levels in the wastewater and grade changes requiring different levels of chemicals. Most correlations are developed using filtered CODs against normal BODs. If this relationship can be established, then a mill could use filtered CODs as a control for setting nutrient feed rates.

Some mills are starting to look at and use on-line COD analyzers. If they are reliable, then a ratio can be used based on the continuous COD reading to control the nutrient feed as shown in the diagram.

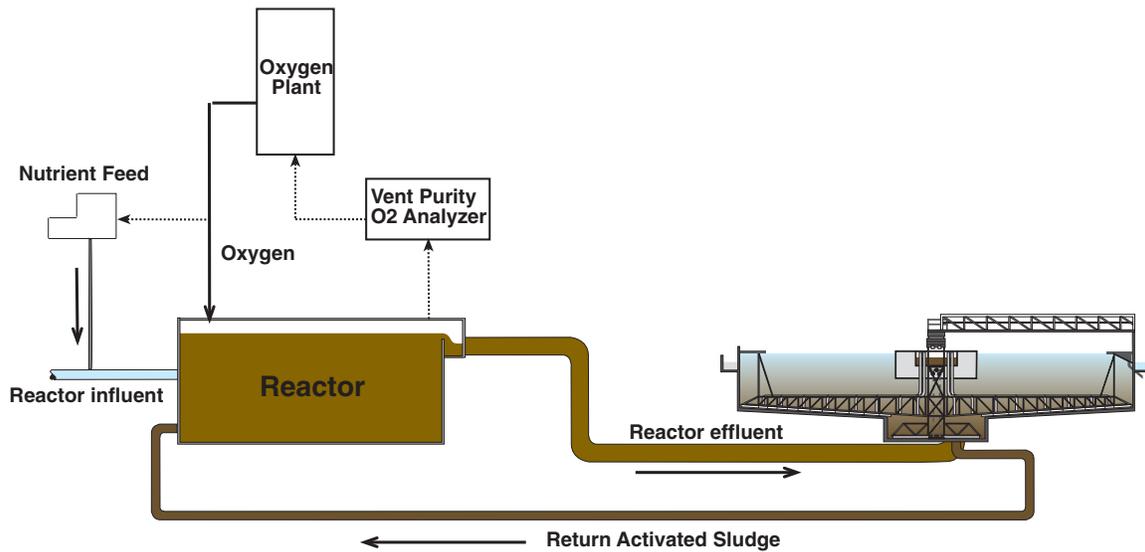


### 5.3.3 TOC

This stands for total organic carbon using a special type of analyzer. Some mills are using on-line TOC analyzers to determine the incoming organic load. Then they set up a ratio from which they can use the TOC concentration to pace their nutrient feed rates as shown in the diagram. The successful mills utilize a good filtering system otherwise the sample tubes become plugged and samples do not reach the analyzer.

### 5.3.4 Pure Oxygen Reactor Oxygen Flow

Pure oxygen reactors are like an on-line respirometer. When the organic loadings change, the oxygen level changes as the bacteria produce more carbon dioxide. This changes the vent purity measured in the last stage of a reactor train. The oxygen flow then changes in order to meet the vent purity set-point. The oxygen flow could be used to pace the nutrient feed rates since it represents the organic loading based on oxygen utilization by the bacteria.



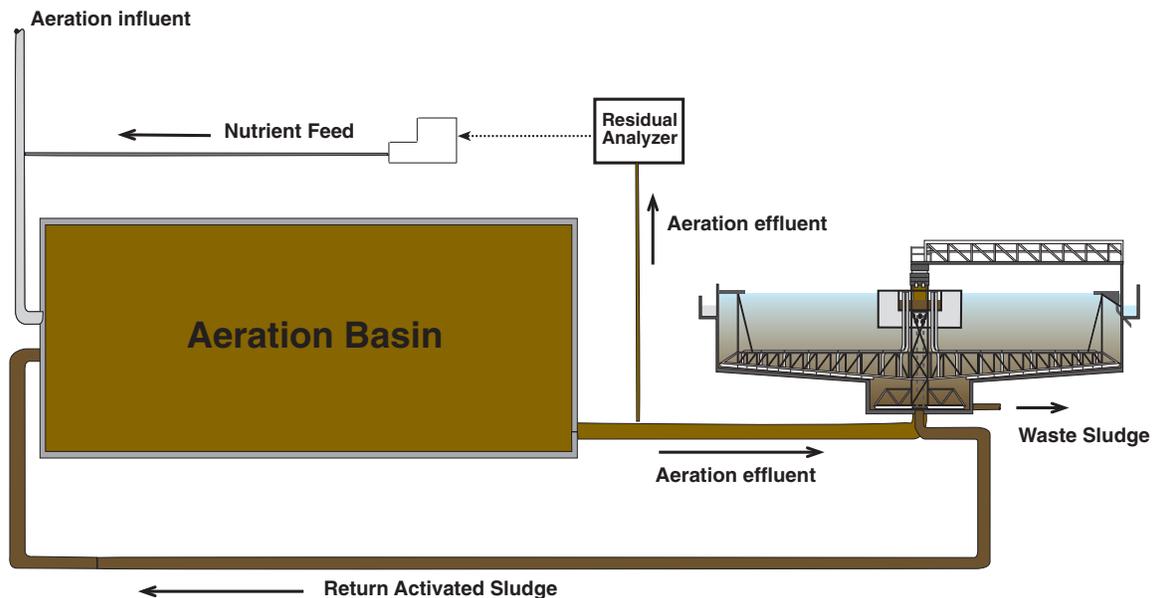
**Pros:** Real time pacing of nutrient feeds to the organic loading. Cost savings will be realized by matching nutrients to the organic load. This strategy will reduce overfeeding or underfeeding nutrients and allow the nutrient residuals to stabilize accordingly.

**Cons:** Strategy will not be effective if BOD correlations to COD, TOC or 1-day BOD cannot be established or are not stable. The correlations should be validated frequently as they may show variations, especially seasonal variations.

#### ***5.4 Control to On-line Continuous Residual Measurement***

Residual analyzers can be used to control nutrient feed rates since they are proving to be more reliable and requiring less maintenance and cleaning. Use of residual analyzers by the Canadian paper industry has been fairly limited. The main analyzers being used are for ammonia and orthophosphate. These residuals are measured in the filtered aeration basin effluent.

This strategy uses nutrient residual measurements to pace the nutrient feed rates as shown in the following diagram. The diagram shows the nutrient residual signals sent to the nutrient feed controllers to set the nutrient feed rates. The continuous measurement allows mills to pace the nutrient feed rates based on the residual targets versus the measured residuals.



**Pros:** Eliminates periods of low and high residuals because the nutrient feed rates are adjusted more frequently than the once per day adjustments that are more common when using manual measurements. Achieves cost savings through optimized feed rates.

**Cons:** Nitrification usually results in low ammonia residuals and elevated nitrate residuals. This strategy could result in overfeeding nitrogen unless nitrate residuals are routinely checked. Given the detention time in aeration basin and secondary clarifier, the control algorithm may be difficult to define.

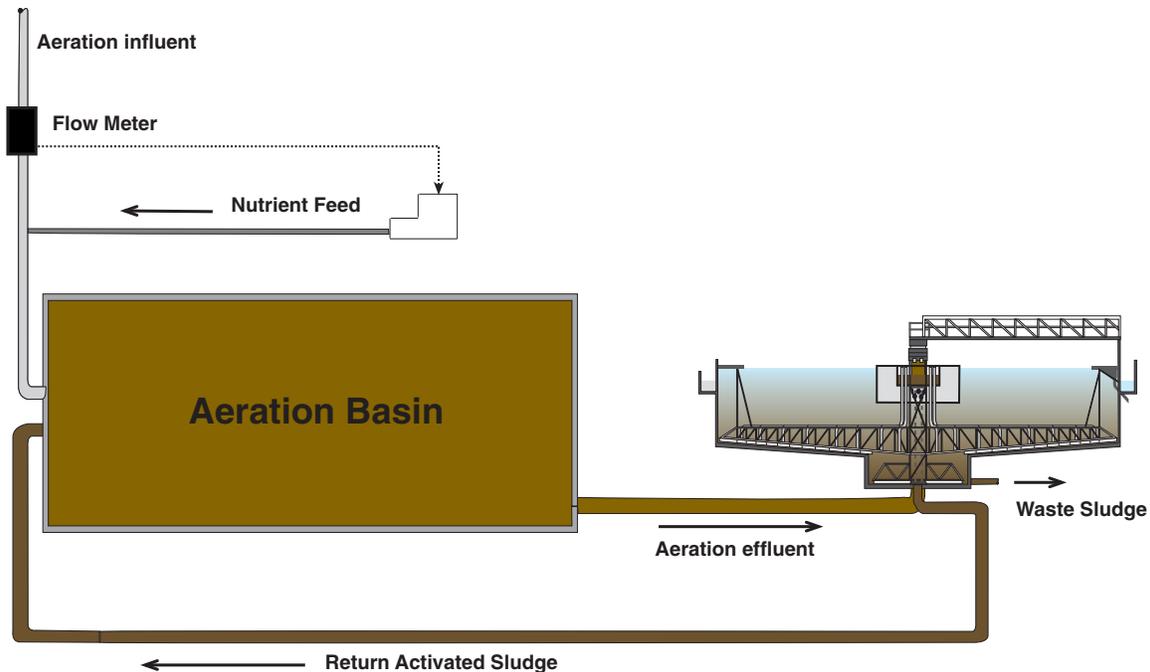
### **5.5 Control to Influent Flow**

Mills where flow rate changes correspond to changes in organic loading could use this strategy. This strategy requires using flow measurement of the aeration influent in place of the final effluent flow. The aeration basin influent flow represents the real time loading to the basin. Final effluent flow has a lag time, which may or may not be significant because of the aeration basin and secondary clarifier hydraulic detention time.

In addition, large primary clarifiers would play an important role in this strategy as they would provide enough buffering to minimize changes in organic concentration while dealing with flow rates changing by as much as 20 – 25%.

So with this strategy, assuming a fairly constant BOD concentration, when flow rates increase, a higher organic load will be sent to the treatment system requiring more nutrients. Lower flow rates mean lower organic loadings and lower nutrient feed rates.

This strategy uses the influent flow rate to pace the nutrient feed rates. The diagram shows the flow signal sent to the nutrient feed controller to set the nutrient feed rates.



**Pros:** Nutrient feed better matches changes in loading based on flow changes.

**Cons:** Strategy may not be as effective if using final effluent flow if the hydraulic lag time in aeration basin and secondary clarifiers is significant. Flow changes may not represent actual organic loading because of changes in concentration.

### **5.5.1 Control to Influent Flow Adjusted by COD/TOC Input**

This strategy takes the influent flow strategy and refines it based on the measured COD/TOC strength of the wastewater. So, if excess water that is low in organics is added or removed from the wastewater flow, the organic concentration will change accordingly.

For example, if COD or TOC is measured on a grab sample every shift, the result can be entered into the control scheme to refine the load calculation. The system would always use the last measurement.

Combining the organic measurement with the wastewater flow rate, the nutrient feed rates will then be paced based on the flow with adjustments made based on the organic content.

**Pros:** Compensates for changes in organic loading independent of flow changes. Can be seen as a fair trade-off with on-line measurements of COD/TOC.

**Cons:** Not as good as on-line monitoring of COD/TOC.

### **5.6 Control to Production**

Some mills feed their nutrients based on their production rate. This would work for mills with a single significant source of the BOD. After determining what percentage production contributes to the BOD loading, BOD loadings are predicted based on the continuously tracked production rate. A database should be maintained to continually analyze the BOD load versus the production rate over a moving period.

Some refinements maybe needed depending on the treatment systems. Time delays should be incorporated to account for primary clarifier and equalization basin detention times before the loading enters the aeration basin.

**Pros:** Matches nutrient feed to the anticipated organic load produces based on production rate.

**Cons:** This strategy will not be effective for mills that have different organic loadings (kg BOD/tonne) for the variety of grades produced. It requires good supporting data to establish correlations. Not effective during transition periods (paper machines/pulp mill shutdown, upsets, etc.) or for multi-grades producers.

### **5.6.1 Control to Production Grade Type**

Some mills are matching BOD loadings to grade type. This means knowing the approximate BOD produced per tonne per grade type. With production grades and schedules known in advance, mills can set the nutrient feed rates to match the incoming BOD load.

**Pros:** Sets nutrient feed rates according to the pulp and paper grades being produced. This more closely matches the nutrient requirements to the incoming organic load.

**Cons:** This strategy will not be effective if the kg BOD/tonne widely varies for each particular grade.

### **5.7 Control of ASB Nutrients**

Nutrient management control strategies are quite different for ASBs. Because of the inherent buffering capacity of ASBs, nutrient deficiency tends to develop over weeks rather than days, so monitoring of residuals several times a week is sufficient to allow for adjusting nutrient feed rates. The longer hydraulic retention times and significant cycling of nutrients through benthic feedback makes it quite difficult to control nutrient addition. One strategy for ASB nutrient management is to monitor soluble BOD or COD, residual ammonia and phosphate at one or more points in the ASB close to where most of the soluble BOD or COD has been taken up, and before benthic feedback becomes a predominant source of nutrients. Operating targets N and P concentrations at these points are mill specific, but are in the range of 0.5 to 1 mg/L for ammonia and 0.5 to 1 mg/L for orthophosphate. Note there is some potential for nitrification and denitrification in ASBs. For this reason, we recommend monitoring TIN rather than just ammonia.

## **6.0 Minimizing Nitrogen and Phosphorus Discharges**

Mills need to evaluate the nutrient forms in the discharge to better understand how to minimize the nutrient levels. This means differentiating between soluble and insoluble, organic and inorganic.

If the soluble fraction is small relative to the total nutrient measured, then the loss of solids is the cause of the nutrients in the discharge. This requires improving solids capture in the secondary clarifiers (AS) or quiescent zones (ASBs) in order to lower nutrient discharges.

If the soluble fraction accounts for most of the nutrient concentration, then the type of nutrient becomes important to determine. Ammonia and orthophosphate are inorganic forms and are the bioavailable forms used by the bacteria for BOD oxidation. If these are present, then either 1) the supplement feed rate(s) are too high, 2) they are being released from microbial decay in a settling zone or basin, or 3) they are being used in mill processes and exceed the microbial requirements.

If the inorganic fraction of the soluble residual nutrients is low, then the nutrients present are in non-bioavailable form and are passing through the treatment system. This requires further investigation to identify where they are coming from and whether they can be better managed within the mill operation. Otherwise, the mill may need to evaluate switching to different process chemicals or modifying production processes to minimize their level discharged to the sewer.

## **6.1 Control Effluent TSS**

Biological solids contain nitrogen and phosphorus. Nitrogen content typically ranges from as low as 6% up to 15% on a dry weight basis. Phosphorus content typically ranges from 0.5 to 2%. So for example, a discharge with 30 mg/L TSS could have a nitrogen contribution of 1.8 mg/L up to 4.5 mg/L and a phosphorus contribution of 0.15 to 0.6 mg/L.

Poor sludge quality will have a big impact on effluent TSS as every mill would attest to. Filamentous bacterial growths, polysaccharide produced from nutrient deficiency or zoogloea, and floc formation problems will result in elevated effluent TSS. It is very important that when there are periods of poor sludge quality, the mill properly identify the cause(s) and eliminate them. Microscopic examinations are key in identifying sludge quality problems.

### **6.1.1 Activated Sludge**

The secondary clarifiers (gravity, DAF) are intended to remove and capture the biological solids before discharging the treated wastewater. With poor sludge quality, the clarifiers are pushed to their limit in trying to capture biological solids. Correcting sludge quality problems will allow the clarifiers to produce quality final effluent.

There are other factors that can affect the clarifier performance efficiency. Some of these factors include hydraulic slugs, high clarifier sludge inventories (not enough wasting, low RAS rates) short-circuiting from unequal weir levels and influent baffle design, lack of scum removal, algae growths on the weirs and launders, and adding too much settling aid resulting a floating sludge layer. If these are occurring then changes are needed. Some of these factors are operational that should be relatively easy to fix. Some of these will require some modifications such as leveling weirs, redesigning the influent baffle and installing a scum baffle and skimmer.

If denitrification occurs in secondary clarifiers and results in significant solids losses, then changes in nitrogen addition, aeration basin operation and RAS rates may be required to correct this problem.

### **6.1.2 ASBs**

Assuming good sludge quality, then most effluent TSS issues are related to the quiescent zone. High sludge accumulation will lead to short-circuiting and solids wash out. If

sludge rises up to the surface because of the gases produced from anaerobic activity, it will wash out in the final effluent.

Installing mixing aerators just prior to the discharge has helped to reduce TSS by breaking up sludge clumps and returning them back towards the quiescent zone. Baffles have been used to help keep sludge accumulations more towards the front half of the ASB and away from the discharge.

Sludge dredging programs may need revising with high sludge accumulation rates. A higher frequency may be needed in order to create volume for the solids to settle out and not escape to the final effluent.

Sludge accumulation is based on the BOD loading as well as the influent TSS. Preliminary and primary treatment may allow additional solids to pass to the ASBs and these should be minimized. BOD loadings should be trended to see if they have increased. If they have changed, determine if it is from increased production or mill operation inefficiencies.

## ***6.2 Properly Manage Supplement Feed Rates***

This is the first place to look when attempting to lower nutrient residuals in the final effluent. More often than not, optimizing feed rates leads to lower nutrients in the final discharge.

1. Make sure to accurately measure residuals. This includes proper sample locations and proper sample handling to prevent nutrient residuals from changing before analyzing.
2. Make sure that small adjustments can be made when adjusting feed rates. Sometimes feed equipment is not sized properly for making small adjustments.
3. Make sure to track nutrient feed through drawdowns, inventory changes, and tracking deliveries. Some mills found nutrient feed problems when product delivery frequencies had changed even though all other nutrient information had not changed significantly.
4. Ensuring operators visually inspect the nutrient feed system(s) to check for leaks and/or blockages.

When changing nutrient feed rates, the residuals should change within 1-2 hydraulic detention times. What takes longer is waiting for the biology to change. Experience says it takes a minimum of 2 – 3 sludge ages for a new biology to develop and up to 5 sludge ages to see the final biology. It is very important to monitor the biology using the microscope to observe new filament growth. It then becomes necessary to identify the filaments because they can grow from different causes outside of nutrient deficiency. India ink stains for observation of nutrient deficient polysaccharide or the anthrone chemical test are also useful in determining nutrient deficiency.

## ***6.3 Change Mill Operations – Use Different Chemicals, Modify Production Processes***

Mill chemicals are constantly changing not only for pulping and papermaking but also for support systems such as boilers and raw water treatment. Many mills have found that

they have been able to lower or even stop adding nitrogen or phosphorus because there were sufficient amounts present in the influent wastewater. But, if the nitrogen or phosphorus is biologically unavailable to the bacteria they will pass through to the final effluent. If biologically available nutrients are added in excess such as phosphoric acid used in boiler water treatment, they will increase the nutrient residual in the final discharge.

If this is the case, then the mill and chemical supplier must work together to find the proper chemical to use for mill operations but not produce elevated nitrogen and phosphorus levels in the final discharge.

### **6.4 Mill Shutdown Impacts**

During mill shutdowns, the bacteria go into endogenous decay mode because of the lack of food. As the cells lyse, nutrients are fed back into the process and leave in the final effluent. This is temperature dependent. If the shutdowns occur during warm weather, more nutrients will be released because of higher activity rates. If the shutdowns occur during the winter, fewer nutrients are released as the activity rates slow down as the aeration basin temperatures drop to lower levels.

The amount of endogenous decay also depends on the length of the shutdown. For short shutdowns for 1 to 3 days, less decay will occur. For shutdowns for 7 to 10 days or longer, more decay will occur. All of this again will depend on the basin temperatures.

To reduce endogenous decay, supplemental food could be fed into the process. Storing wastewater, if possible, is an option. Sewering small amounts of liquor, sewerage prepared starch, sewerage whitewater, etc. are options. Many mills have used molasses as an organic source.

Note that the normal organic load does not have to be fed to the system. Only a portion of the organic load is needed to minimize endogenous decay. As long as the bacteria are kept busy oxidizing organics, endogenous decay can be minimized.

Be careful when supplementing food because this is temperature dependent. Feeding bacteria in cold basin temperatures can lead to permit excursions in BOD and elevated nutrient residuals in the final effluent.

During shutdowns, flows usually drop off to very low levels. So even if nutrient residuals increase, the nutrient load in the final effluent will be quite low compared to a normal operating day. So there may be no need to add supplemental food.

Mills should have specific procedures they use during shutdowns to accommodate for system changes and to facilitate start-ups.

### **6.5 Revise Treatment Plant Operation**

#### **6.5.1 Equalization or Spill Basins**

Shock loads and slug loads impact the biomass making nutrient management very difficult. If the shock load is inhibitory or toxic, the biomass will not process BOD which means nutrients will pass through to the final effluent. If some of the biomass die-off, nutrients will be released increasing the nutrient residuals even higher.

If the shock load or slug load is degradable, nutrients must be increased to try and maintain an acceptable BOD:N:P ratio. After the load passes through, nutrient residuals tend to be high because adjustments to lower feed rates are lagging.

Incorporating an equalization basin will provide some buffering of the slug loads and provide a small degree of treatment as well. Spill basins if properly utilized by capturing and slowly returning suspect wastewater will protect the biomass from inhibition and toxicity thus preventing the release of elevated nutrient residuals in the final effluent.

### **6.5.2 Reroute Side Streams**

If the side streams are adding significant nitrogen or phosphorus, make sure they are being added so that they can be used for biological treatment. If they exceed biological needs, look to see if nutrients can be lowered elsewhere to make the overall addition rate correct for BOD oxidation.

### **6.5.3 Secondary Clarifiers**

Clarifiers with long sludge detention times will more than likely undergo biological activity resulting in the release of nitrogen and phosphorus. These will then pass through into the final effluent.

The actual detention time under which this occurs is affected by temperature. Warmer temperatures will promote faster biological activity rates so shorter detention times would be needed to minimize their release. Cooler temperatures slow down activity rates so it would take longer for this to occur.

## **6.6 Physical Treatment Plant Changes**

### **6.6.1 Activated Sludge**

Activated sludge aeration basins usually will experience release of nutrients from endogenous decay if they have long detention times or are operating at low F/M conditions.

**Step Feed.** Endogenous decay is an internal recycle of nutrients that can be a good thing. But if the endogenous decay occurs later in the basin after BOD removal has occurred, then the nutrients will not be used and will pass out of the basin. Sending a small portion of wastewater further into the basin will keep the bacteria working and using nutrients while oxidizing BOD. This can be done with multiple feed points depending on the size of the basin. Keeping the bacteria active in oxidizing BOD limits the amount of endogenous decay that can occur.

**F/M.** Low loaded treatment systems will have endogenous decay occurring in the aeration basin. If the bacteria do not recycle the nutrients for BOD removal then they will pass to the final effluent. Raising the F/M should lower the degree of endogenous decay that will occur. However, in narrow plug flow basins, the loading at the front of the basin may get too high resulting in sludge quality problems from zoogloal growth or filamentous bacterial growth. If adjusting the F/M creates sludge quality problems, then consider redistributing the wastewater using step feed to maintain good sludge quality but minimize the endogenous decay.

### **6.6.2 ASBs**

The most successful ASBs take advantage of the benthic feedback of nutrients into the aerobic liquid phase where BOD oxidation takes place. This means they have a balance

of allowing settling and sludge digestion to occur under the aerobic liquid phase instead of having separate aerated zones followed by solids capture zones. Many mills were designed with more than one cell where the first cell is completely mixed and aerated with the second cell partially aerated up front followed by the quiescent zone for solids capture just prior to final discharge.

The biggest problem with the separate treatment phases is the release of nutrients from the sludge settling zones just prior to the final discharge. However, there are a few options to incorporate to reduce nutrient levels in ASB final discharges. These include, step feed, recirculation and reconfiguring mixing/aeration.

**Step Feed.** This option involves sending some wastewater down towards the zone where nutrients are being released. This maybe located later in the aeration zone where endogenous decay occurs. It most certainly will be near the beginning of the quiescent zone where nutrients are being fed back from anaerobic decay. By adding BOD, bacteria will utilize the released nutrients as they metabolize the BOD. The caution is not to overfeed the wastewater where it passes though in the final effluent untreated.

This option may require placement of an aerator in or near the quiescent zone to supply some oxygen for the bacteria as they oxidize the BOD. Mills must make sure to leave time and volume for the biological solids to settle out before the discharge.

**Effluent Recirculation.** This option involves sending a portion of the effluent back to the influent of the ASB. With this option, nutrients are recycled back to be used by the bacteria thus lowering nutrient feed rates. This option also dilutes the incoming wastewater to lower concentrations. Mills have done this by either sending effluent back from the first cell or from the final discharge. Usually the final discharge has the higher nutrient levels.

**Mixing/Aeration.** This option requires repositioning aerators to reduce the mixing horsepower at the influent end of aerated ASBs. This allows solids to settle out and create the benthic sludge layer. The bacteria then use nutrients released from the benthic layer as they continue to oxidize BOD. Aerators can be repositioned further downstream to provide more oxygen yet still provide low mixing intensity and allow solids to settle out before discharge.

## ***6.7 Incorporate Nutrient Removal Processes If Needed***

If treatment plant operational changes, mill operational changes, physical treatment plant changes can not be done or are ineffective, then nutrient removal processes<sup>[7]</sup> maybe required to lower nutrient levels in the final discharge. Implementing nutrient removal processes requires wastewater treatment nutrient removal expertise to help determine if it is feasible and what are the best options.

Phosphorus can be removed through chemical precipitation or through biological uptake. Adding a metal salt such as alum or a ferric chemical in proper ratio to the phosphorus residuals will precipitate it out. Biological phosphorus removal is more involved as it requires an anaerobic treatment step in sequence with the aerobic step. If this is not done properly, the biological uptake of phosphorus will not occur. Biological phosphorus removal is not readily practiced in mill treatment systems because other changes have proven to be adequate in lowering phosphorus residuals.

Ammonia can be converted to nitrate through nitrification. This requires more oxygen and longer sludge ages to allow the slow growing nitrifiers to grow. This typically occurs in mills that overfeed nitrogen. Removing ammonia lessens the impact on receiving water from oxygen depletion and toxicity but nitrate can promote algae growth, which is not desirable. This would require a denitrification step to allow nitrate respiration to occur. This step is ahead of the aerobic treatment step where the bacteria utilize nitrate (nitrate or anoxic respiration) as they start oxidizing BOD. This option requires specific anoxic zone separate from the aerobic zone. Biological nitrogen removal is not widely practiced in mills except at ammonia based mills that use a combination of nitrification-denitrification to lower the ammonia and nitrate residuals in the final effluent.

If mills are not sure if nutrient removal is needed, hire some outside experienced expertise to sort through the various options. Maybe it only requires in plant or in mill modifications to achieve minimal nutrient levels in the final effluent.

## 7.0 Implementation

Implementing this BMP requires additional focus for operators, developing operating plans and targets and monitoring and fine-tuning treatment plant operations and control plans.

### 7.1 Operator training

Operators need a thorough understanding of nutrients, where they originate from and how they can be controlled. Proper nutrient management and control is the foundation for maintaining low nutrient residuals. The challenge is maintaining good sludge settling characteristics that will produce a final effluent low in suspended solids, which helps reduce nitrogen and phosphorus discharges.

A training program should be developed for operators covering all aspects of nutrient management and how it applies to them. The training topics could closely follow your newly developed BMP so that the operators understand the need for nutrients, sources of nutrients, how to manage nutrient feed rates, how sampling and analysis techniques can affect the residuals, and how to use the nutrient operating plan established for the plant.

### 7.2 Developing an Operating Plan and Targets

After addressing and incorporating all of the factors affecting nutrients in the final discharge, mills should establish an operating plan for their treatment plant and mill operation. The plan should include the sampling protocols, residual analyses, and calculation of the BOD:N:P ratio versus target. Make sure to include residual targets that operators can control to.

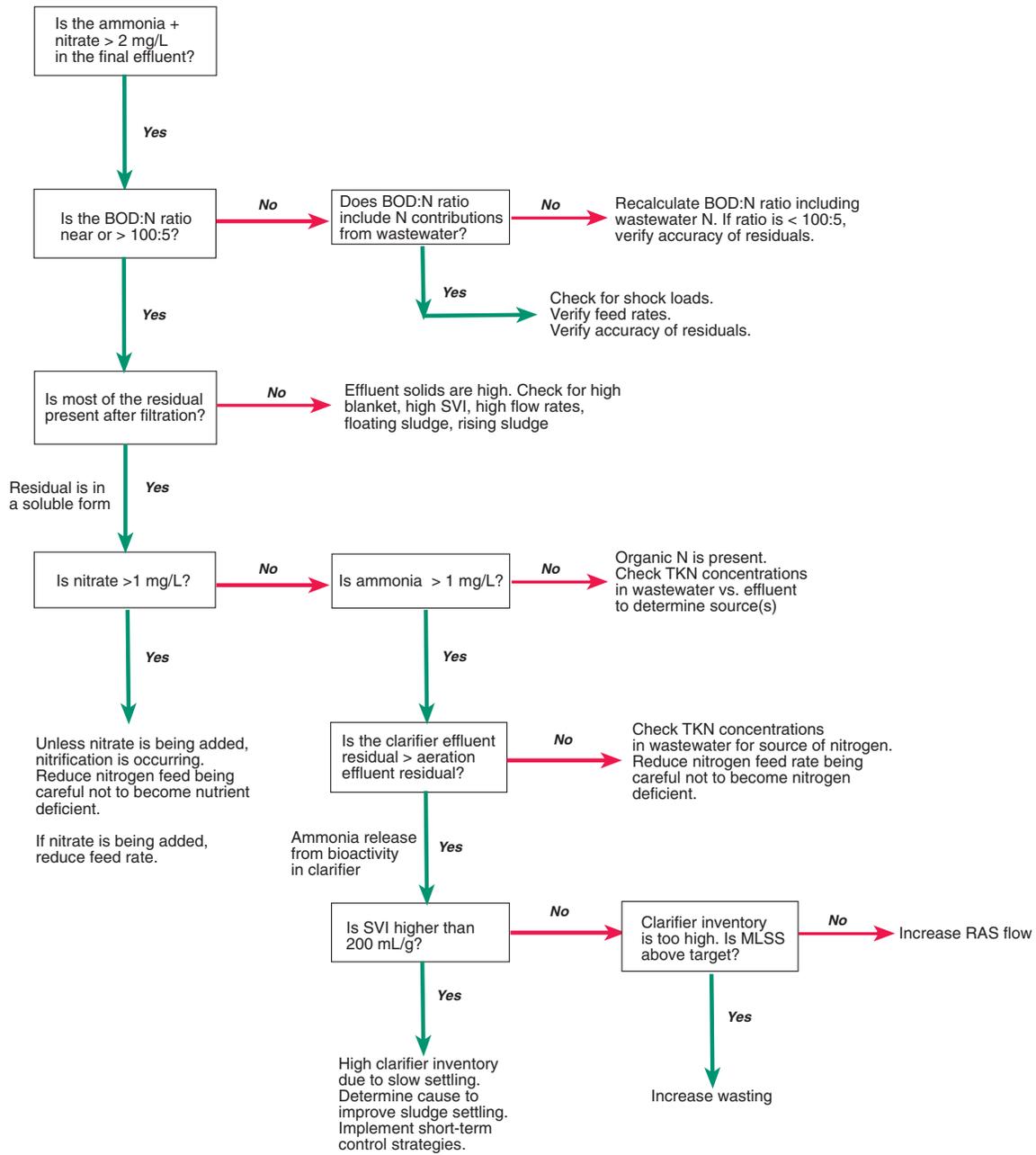
Through proper training on nutrients and on the operating plan, the operators should be able to operate the treatment plant to achieve good effluent quality while still minimizing nutrient residuals in the final effluent.

#### 7.2.1 Managing Nitrogen and Phosphorus Decision Keys

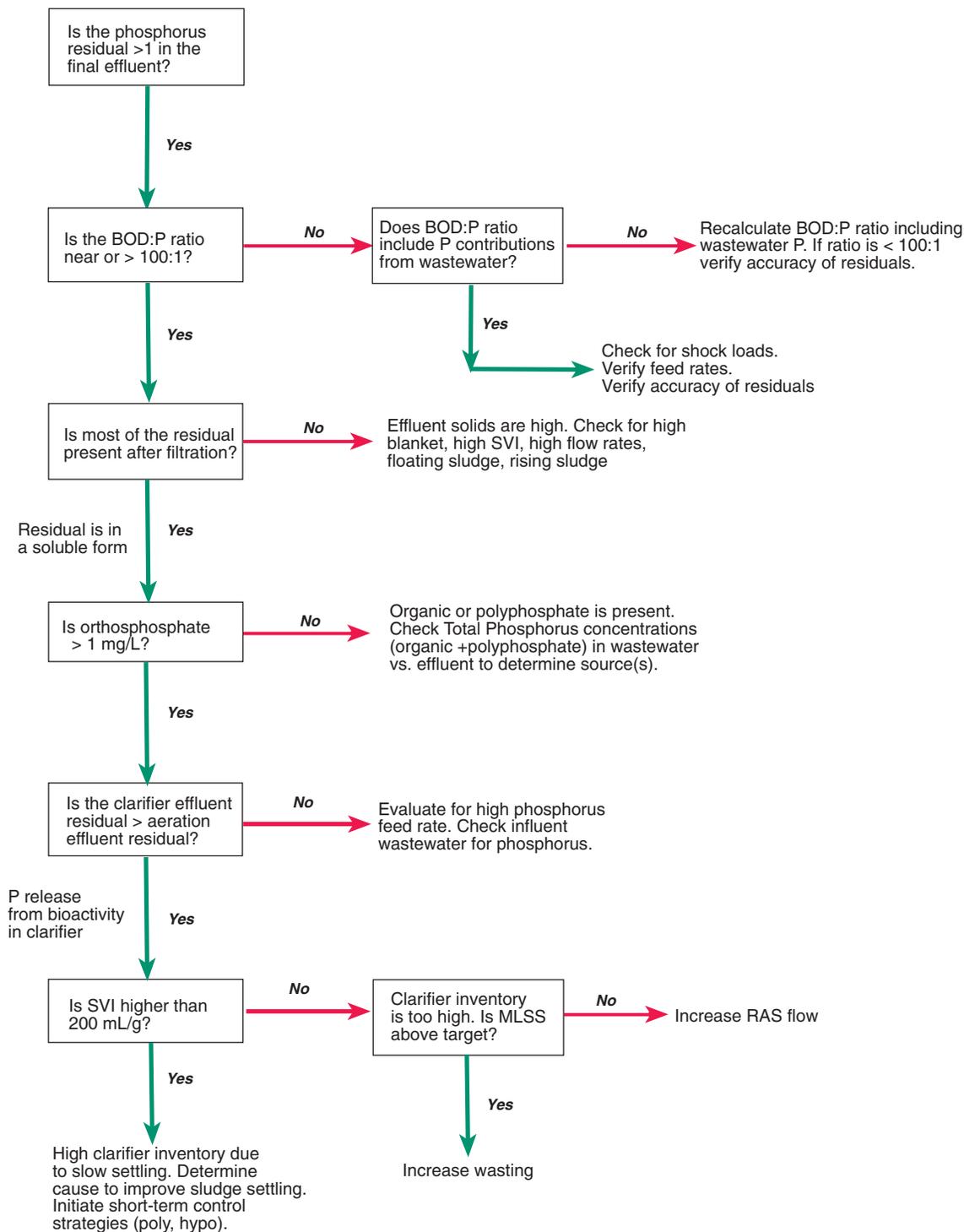
The following decision keys <sup>[5]</sup> are site-specific examples from mill treatment systems managing nutrients. There is one decision key for managing nitrogen and one for managing phosphorus for both an activated sludge system and an ASB system. These

represent different approaches that mills use to successfully manage their nutrients.

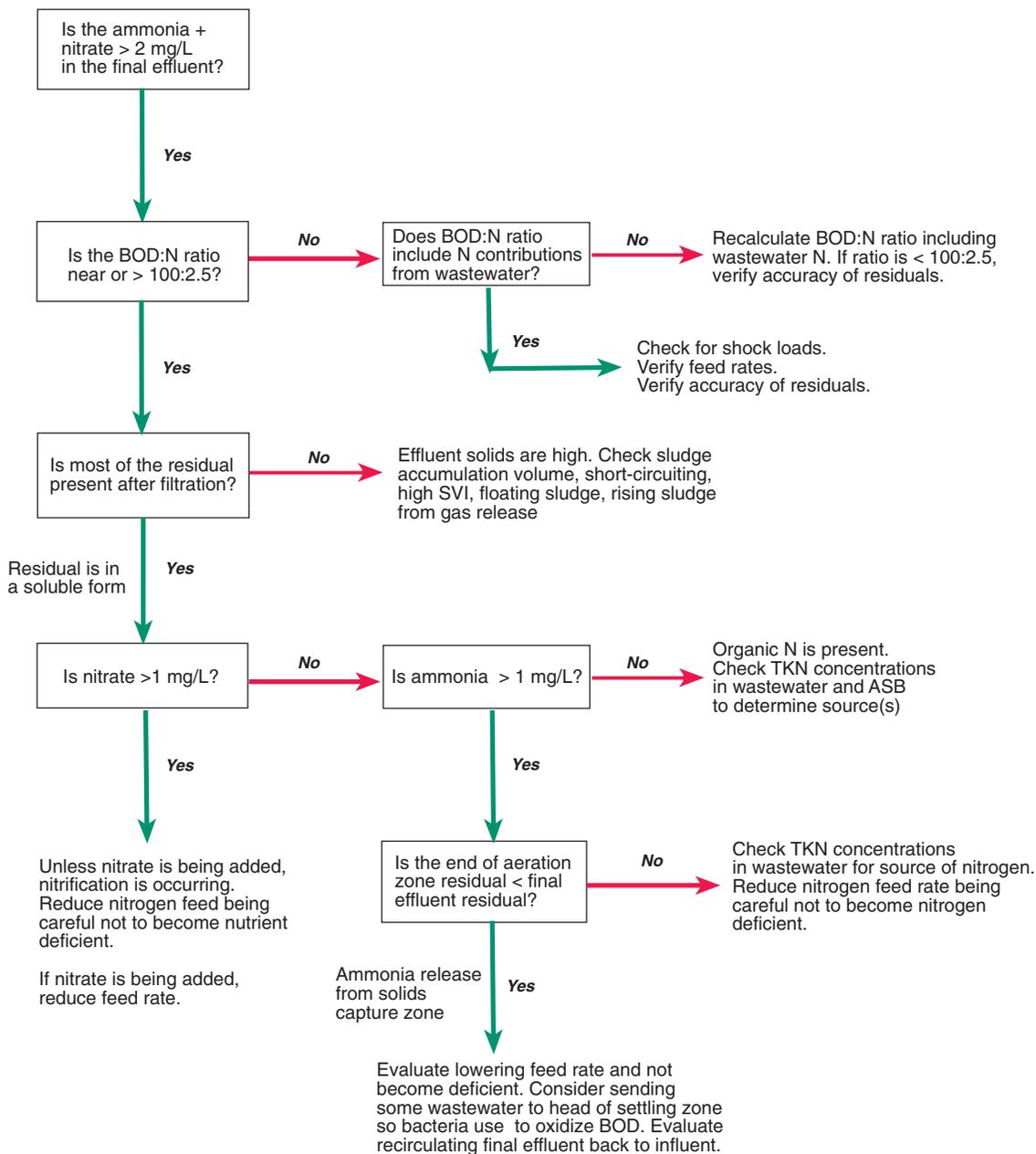
# Nitrogen Decision Key Example



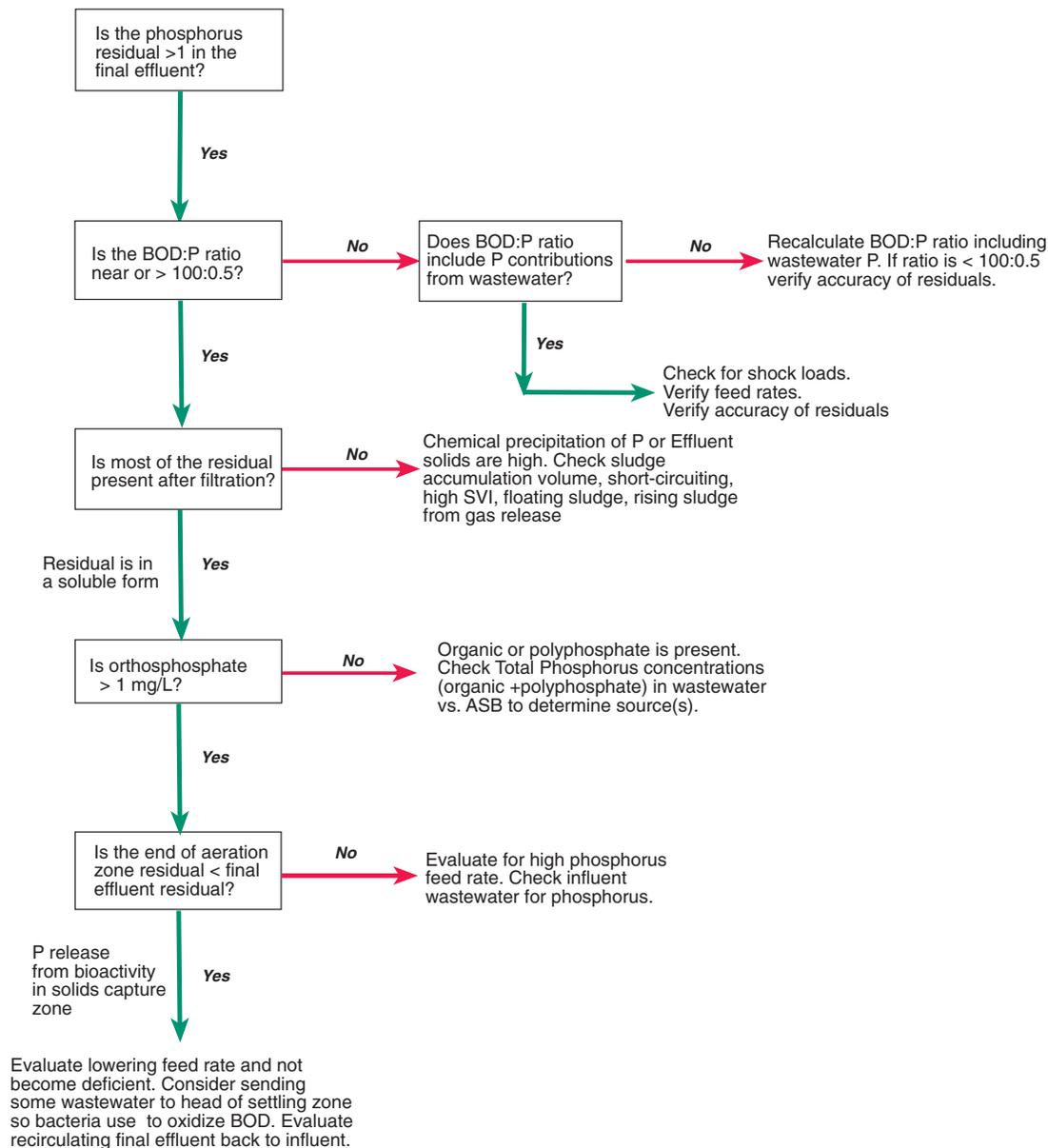
# Phosphorus Decision Key Example



# ASB - Nitrogen Decision Key Example



## ASB - Phosphorus Decision Key Example



The following is an example of how a mill established their nutrient management plan. This is a paper mill with a 5-hour aeration basin hydraulic detention time.

- 1) Established a database of the nitrogen and phosphorus levels in the influent wastewater to secondary treatment.
- 2) Calculated and continuously tracked the BOD:N:P ratio.
- 3) Matched effluent nutrient residuals measurements against the BOD:N:P ratio to help define the site-specific ratio.
- 4) Developed a COD:BOD correlation.
- 5) Developed a statistical database on COD loadings based on paper grades produced.
- 6) Each day predicted the organic loading based on paper grade(s) produced. From the spreadsheet, they determined the urea feed rate and phosphoric acid feed rate to meet established target BOD:N:P ratio.
- 7) Used nutrient residuals to verify and refine the nutrient feed rates.

### **7.3 Fine-tuning**

Establish a baseline knowing what the nutrient forms are in the mill effluent, side streams, from nutrient addition and nutrient release from within the treatment plant.

To lower the nitrogen and phosphorus in the final discharge, first determine what forms of nitrogen and phosphorus are being discharged. Second, determine the soluble versus total fractions. If it is soluble, then look at your nutrient addition program. It is very likely that excess nutrients are being added. Make sure to profile the treatment plant to determine if the soluble nutrients are coming in the influent or being generated or released within a treatment unit because of cell decay. If they are present in the influent, the mill needs to identify the sources. If the soluble nutrients are being generated in a treatment unit, either operational adjustments are needed or possibly some physical changes are needed.

If the total nitrogen or total phosphorus is high relative to soluble N and P, more than likely it is from elevated solids in the discharge. Determine if the solids are suspended solids or dissolved solids. If they are suspended solids, then evaluate the solids settling characteristics and the settling basin performance (clarifier or settling zone in ASBs). A settling aid might be required to help capture the solids and keep them out of the effluent. Changes will be needed if sludge quality is poor.

If the solids are dissolved solids, look upstream to the mill first to see what the contribution is. Better solids retention in the mill may solve the high dissolved solids problem in the final effluent. If the dissolved solids are from a side stream, additional treatment of the side stream may be needed.

## **Appendices**

### **A. Ammonia Concentration vs. pH Table**

The form of ammonia (ionized vs. un-ionized) is dependent on pH. The following table shows the concentration of ammonia it takes to produce 0.5 mg/L of NH<sub>3</sub>-N. Note that as the pH rises above 7 towards 8, the amount of ammonia to produce NH<sub>3</sub>-N decreases. At a pH above 8, it does not take a very high ammonia residual to become the toxic un-ionized form NH<sub>3</sub>-N.

<b>pH</b>	<b>Total Ammonia at 15°C that produces Un-ionized Ammonia of 0.5 mg/L</b>
7.0	184
7.1	146
7.2	117
7.3	93
7.4	74
7.5	59
7.6	47
7.7	37
7.8	30
7.9	24
8.0	19
8.1	15.1
8.2	12.2
8.3	9.7
8.4	7.8
8.5	6.3
8.6	5.1
8.7	4.2
8.8	3.4
8.9	2.8
9.0	2.35

Reference: U.S. Environmental Protection Agency. 1979. Aqueous Ammonia Equilibrium – Tabulation of Percent Un-ionized Ammonia Species. EPA 79-091. U.S. EPA. Springfield, VA.

## B. Commonly Utilized Nutrient Methods

Method Approach	Methods	General Working Range	Reported Interferences
<b>Ammonia</b>			
Distillation	MA.300-N1.1, MA 303-N1.0, BC NH <sub>3</sub> , EPA 350.1, SM 4500 NH <sub>3</sub> B, USGS 973.49	Dilution Dependent	
Colorimetric Automated Phenate (Berthelot)	BC NH <sub>3</sub> (Berthelot), EPA 350.1, SM 4500 NH <sub>3</sub> G and H, ATG#4a,	0.01 to 2.0 mg NH <sub>3</sub> – N/L	Sulphide, turbidity, color, magnesium and calcium
Colorimetric Manual Phenate (Berthelot)	ATG#4a, SM 4500-NH <sub>3</sub> F, EPA 350.2	0.05 to 1.0 mg NH <sub>3</sub> – N/L	Sulphide, turbidity, magnesium and calcium, color
Colorimetric Automated Salicylate	MA.300-N1.1, MA 303-N1.0	0.05 to 0.25 mg NH <sub>3</sub> – N/L, 0 to 2.0 mg NH <sub>3</sub> – N/L	Color, turbidity, nitrates >10 mg/L, cyanates
Ammonia selective electrode	ATG#4a, BC NH <sub>3</sub> (ion selective electrode), EPA 350.3, SM 4500-NH <sub>3</sub> D or E(19th), 4500-NH <sub>3</sub> F or G(18th), ASTM D 1426-98, 03(A)	0.05 to 1400 mg NH <sub>3</sub> – N/L	Volatile amines, mercury, silver
Titration	ATG#4a, EPA 350.2, SM 4500-NH <sub>3</sub> C(19th), SM 4500-NH <sub>3</sub> E(18th)	5 to 100 mg NH <sub>3</sub> – N/L	Color, turbidity
Nesslerization	EPA 350.2	0.5 to 10 mg NH <sub>3</sub> – N/L	Aromatic and aliphatic amines, turbidity, cyanates
Ion Chromatography	ASTM D6919-03, ATG#4a	0.4 to 10 mg NH <sub>3</sub> – N/L	Substances with similar retention times
<b>Nitrate/Nitrite</b>			
Colorimetric, Cadmium Reduction, Manual	BC (NO <sub>3</sub> +NO <sub>2</sub> , Cd reduction, manual), ATG#4b, EPA 353.3, SM 4500-NO <sub>3</sub> -E, ASTM D3867-99(B)	0.01 to 1.0 mg (NO <sub>3</sub> /NO <sub>2</sub> )-N/L	Turbidity, color, oil and grease, iron, copper or other metals, chlorine
Colorimetric, Cadmium Reduction, Automated	BC (NO <sub>3</sub> +NO <sub>2</sub> , Cd reduction, auto), EPA 353.2, SM 4500-NO <sub>3</sub> -F, D3867-99(A)	0.05 to 10 mg (NO <sub>3</sub> /NO <sub>2</sub> )-N/L	Turbidity, color, oil and grease, iron, copper or other metals, chlorine
Colorimetric, Automated Hydrazine	MA.303-NO <sub>3</sub> 1.0, MA.300-NO <sub>3</sub> 1.0, ATG#4b, SM 4500-NO <sub>3</sub> -H,	0.02 to 2.0, and 0.01 to 10 mg (NO <sub>3</sub> /NO <sub>2</sub> )-N/L	Sulphide ion, color, turbidity
Ion Chromatography (Nitrate)	BC (nitrate, IC), ATG#4b, EPA 300.0, SM 4110B, ASTM D 4327-97,	0.04 to 13.0 mg (NO <sub>3</sub> /NO <sub>2</sub> )-N/L	Substances with similar retention times

(Continued on next page.)

## B. (Continued)

Method Approach	Methods	General Working Range	Reported Interferences
<b>Orthophosphate</b>			
Automated colorimetric (ascorbic acid)	BC (orthophosphate, dissolved), MA.303-P 1.0, EPA 365.1, SM 4500 PO <sub>4</sub> - F,	0.01 to 1.0 mg P/L, 0.001 to 10 mg P/L (SM)	Color, turbidity, arsenate, barium, lead and silver
Manual colorimetric (ascorbic acid)	EPA 365.2 and 365.3, SM 4500 PO <sub>4</sub> - E	0.01 to 0.5 mg P/L, 0.01 to 2.0 mg P/L	Color, turbidity, arsenate
Ion Chromatography	EPA 300.0, 300.1, SM 4110B	0.01 to 23 mg P/L	Substances with similar retention times
<b>Total Phosphorus</b>			
Persulfate Digestion	See orthophosphate colorimetric methods for analysis MA.315-P1.0, BC (total phosphorus), ATG #6, EPA 365.1, EPA 365.2, EPA 365.3, SM 4500 P B,	0.003 to 1.0 mg P/L, 0.01 to 20 mg P/L	Color, turbidity, arsenate, barium, lead and silver
Kjeldahl Digestion	MA.300-NTPT 1.1, ATG #6, EPA 365.4, ASTM D515-88(B),	0.01 to 20 mg P/L	Color, turbidity, arsenate
<b>Total Kjeldahl Nitrogen</b>			
Colorimetric Automated Phenate (Berthelot)	EPA 361.1, SM 4500 N <sub>org</sub> B (macro) or C (semi-micro)	0.05 to 2.0 mg N/L	Iron and chromium
Colorimetric Semi-automated block digester	EPA 351.2, SM 4500 N <sub>org</sub> C	0.1 to 20 mg N/L	High nitrate levels,
Titration	EPA 351.3	1 to mg N/L	Color, turbidity
Nesslerization	EPA 351.3, SM 4500 N <sub>org</sub> B or C	0.01 to 1.0 mg N/L	Aromatic and aliphatic amines, turbidity, cyanates
Ion Selective Electrode	EPA 351.3, EPA 351.4	0.05 to 1400 mg N/L, 0.03 to 25 mg/L	Volatile amines, mercury, silver
<b>Total Nitrogen</b>			
Combustion and Chemiluminescence Detection	BC (Total and Dissolved N)	0.05 to 0.5 mg N/L	High TOC, HCL,
Alkaline persulphate oxidation	MA 303-N tot 1.0, BC (Total and Dissolved N), USGS I-2650-03/4650-03	0.02 to 1.0 mg N/L, 0.1 to 5.0 mg N/L	Mercury, copper, color, turbidity

With permission – [Table 3.1 Commonly Utilized Nutrient Methods](#), Technical Bulletin No. 937, July 2007, National Council For Air And Stream Improvement (NCASI), Research Triangle Park, NC.

## **C. Acronyms**

AS - activated sludge

ASB - aerated stabilization basins

BOD - biochemical oxygen demand

COD - chemical oxygen demand

F/M - food to microorganism ratio

DAF - dissolved air flotation

OAS - oxygen activated sludge

SBR - sequencing batch reactor

TOC - total organic carbon

TSS - total suspended solids

EEM – Environmental Effects Monitoring

TIN – Total Inorganic Nitrogen

TKN – Total Kjeldahl Nitrogen

## References

1. Barnes, D, Bliss, P.J. 1983. *Biological Control of Nitrogen in Wastewater Treatment*, New York: E. & F. Spon, Ltd.
2. Lowell, RB, Ring B., Pastershank G., Walker S., Trudel, L., and Hedley K., 2005. *National Assessment of Pulp and Paper Environmental Effects Monitoring Data: Findings from Cycle 1 through 3*, Environment Canada, National Water Research Institute, Burlington, ON, NWRI Scientific Assessment Report Series No. 5, 40 p.
3. Marshall, R. 1999. *Industrial Activated Sludge Operations*. Corvallis, OR: Marshall Environmental Training & Consulting (METC) Group, Inc.
4. Marshall, R. 2005. *Aerated Stabilization Basin Operations*. Corvallis, OR: Marshall Environmental Training & Consulting (METC) Group, Inc.
5. Marshall, R. Client communications.
6. Metcalf and Eddy, Inc. 1991. *Wastewater Engineering, Treatment, Disposal and Reuse*, 3<sup>rd</sup> Ed. New York: McGraw-Hill.
7. National Council for Air and Stream Improvement, Inc. (NCASI). 2001. *Selected pulp and paper experience with the control of nutrients in biologically treated effluents*. Technical Bulletin No. 826. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.
8. National Council for Air and Stream Improvement, Inc. (NCASI). 2007. *Synthesis of NCASI information on the management of nutrients for biological treatment of pulp and paper mill wastewaters*. Technical Bulletin No. 937. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.
9. National Council for Air and Stream Improvement, Inc. (NCASI). 2001. *Nutrient forms in Pulp and Paper Mill Effluents and Their Potential Significance in Receiving Waters*. Technical Bulletin No. 832. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.
10. National Council for Air and Stream Improvement, Inc. (NCASI). 2004. *Biodegradability of Organic Nitrogen and Phosphorus in Pulp Mill Effluents*. Technical Bulletin No. 879. Research Triangle Park, N.C.: National Council for Air and Stream Improvement, Inc.
11. Paice, Michael, Liu, Jianrong, Cook, Roger, 2007. *Paprican Special Report PSR 583 Nutrient Management Practices for Effluent Treatment in the Canadian Pulp and Paper Industry*.
12. Richard, M.G. and Cummins, C.K. 1997. Results of phosphorus minimization studies for pulp and paper mill activated sludge systems located around the Great Lakes. In *Proceedings of the 1997 TAPPI International Environmental conference*, 1003-1006, Atlanta, GA. Tappi Press.
13. Sawyer, Clair N., McCarty, Perry L., Parkin, Gene F. 1994. *Chemistry for Environmental Engineering*, New York, McGraw-Hill.