

NITRIFICATION INHIBITION BY QUATERNARY AMMONIUM COMPOUNDS IN WASTEWATER FROM SMALL COMMUNITIES AND SCHOOLS

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ABSTRACT

Quaternary ammonium compounds (QAC) are used extensively in many different types of products. They are rated as nontoxic but are inhibitory, if not toxic at very low levels to nitrifying bacteria. Examples of typical QAC products and their use are discussed in the paper. The best approach to prevent inhibition of nitrification where nitrogen is a prime concern in wastewater discharges is to prevent or remove the QAC before it gets into the wastewater. However, this is frequently not practical. The complications of removing QAC in a treatment system are magnified because it is very slow to biodegrade and very little is known of its degradation rate. Several approaches to treating QAC are presented with examples given. It is concluded that treatment is possible with the methods outlined and detailed designs are difficult because of the lack of degradation rates.

KEYWORDS: Quaternary ammonium compounds, nitrification inhibition

INTRODUCTION

The Problem

Quaternary ammonium compounds (QAC) are nontoxic; however, they will completely inhibit nitrification at very low concentrations of 2 mg/L or less. The effects of inhibition is most predominate in smaller treatment plants where dilution of the QAC is not as prevalent as it is in larger treatment plants. Typically nitrification inhibition is most often seen in plants that are less than 100,000 gpd. The reason for poor nitrification is frequently not understood by trouble shooters attempting to solve the problem for their plant of not meeting the nitrogen discharge limits because they are not familiar with the effects of QAC inhibition properties.

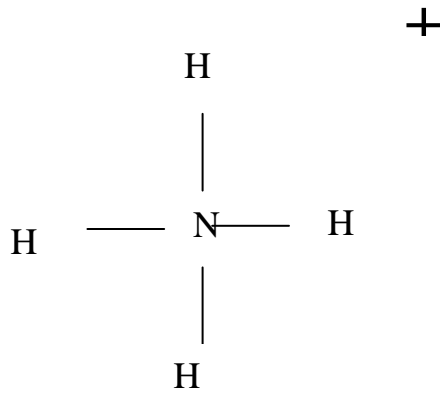
The problem of nitrification inhibition has increased significantly over the past few years because of the rapidly increased use of QAC over the past five to ten years. And, it continues to be used in more and more products. See Table 1 for a partial list of products where QAC is commonly found. Products on Table 1 were found using internet searches for QAC. It is interesting to note that the products in Table 1 range from hand soaps to preservatives that are frequently used by many people without thinking about what is in contact with their skin or being eaten. Based on the products shown on Table 1 it is easy to understand why QAC can be expected to be found in wastewaters where there is little industrial component. It can also be expected in wastewaters where there is an industrial component such as strip-malls, grocery stores, and schools where sanitizers are used to a significant extent.

Table 1. Type of Products Containing QAC

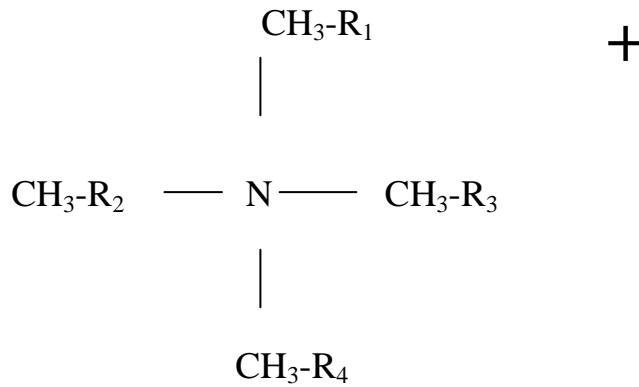
- Acid cleaners
- Antistatic agents
- Body piercing skin preparation
- Car rinsing agents
- Cosmetic materials
- Detergents
- Diagnostic reagents
- Disinfectant cleaners
- Disinfectants
- Fabric softeners
- Fermentation products
- Functional cationics
- Hair cosmetic products
- Hand sanitizers
- Hand soaps
- Industrial cleaners for surfaces
- Oil emulsions
- Ophthalmic solutions
- Pharmaceutical products
- Preservatives
- Sanitizers – for restaurants, bars, paper and chemical supplies, and processing dairy or meat
- Textile softeners
- Thickeners
- Vehicle cleaners
- Water based alkaline degreasers
- Wood preservatives

One of the main problems in determining if a product contains QAC is that there are many different QAC compounds used and they seldom contain the term “quaternary ammonium” on their labels. Quaternary ammonium compounds are derived from ammonium (NH_4^+) by replacing the four hydrogen atoms with organic radicals. The organic radicals are typically made up of long carbon chains and usually contain 12 to 18 carbon atoms. Figure 1 shows a diagram of a simple ammonium ion and a quaternary ammonium ion. Notice that the QAC ion has all four bonds on the nitrogen atom joined to a radical where the hydrogen atoms were. Each of the radicals shown on Figure 1 can be different which makes the QAC have different characteristics.

Table 2 shows some examples of QAC chemicals found using internet searches. Note that QAC compounds frequently contain ammonium chloride or ammonium bromide along with one or more long chain compounds that can only be understood by most wastewater engineers by using a chemical dictionary. It is hoped that Table 2 will help to evaluate if a product has QAC or not by understanding some general types of QAC chemicals and comparing them with those



A. Ammonium Ion



B. Quaternary Ammonium Ion

Figure 1. Diagram of an Ammonium Ion and a QAC Ion

Table 2. Examples of QAC Chemicals

- Alkyl dimethyl benzylammonium chloride
- Alkyl trimethyl ammonium bromide
- Alkylbenzyl dimethyl ammonium chloride
- Alkylpolyglycoether ammonium methyl chloride
- Alkylpolyglycoether ammonium methyl sulfate
- Behenyl trimethyl ammonium chloride
- Benzalkonium chloride
- Benzyl(hydrogenated tallow alkyl)dimethyl, chlorides
- Benzyl-C8-18 alkyldimethyl, chlorides
- Benzylcoco alkyldimethyl, chlorides
- Benzyl dimethyl tallow alkyl, chlorides
- Bis(hydrogenated tallow alkyl)dimethyl, chlorides
- Cetalkonium chloride
- Cetyl ethyl dimethyl ammonium bromide or hexadecyl ethyl dimethyl ammonium bromide
- Cetyl trimethyl ammonium bromide or hexadecyl trimethyl ammonium bromide
- Cetyl trimethyl ammonium chloride or hexadecyl trimethyl ammonium chloride
- Coco alkyl[(2,4-dichlorophenyl)methyl]dimethyl, chlorides
- Coco alkylbis(hydroxyethyl)methyl, chlorides
- Dicoco alkyldimethyl, chlorides
- Dicocoalkyldimethyl ammonium chloride
- Distearyl dimethyl ammonium chloride
- Ditallowdimethyl ammonium chloride
- Dodecyl trimethyl ammonium chloride or lauryl trimethyl ammonium chloride
- Hexadecyltrimethyl ammonium chloride
- Hydrogenated tallowtrimethyl-ammonium chloride
- Iodophor
- Lauralkonium chloride
- Lauryl trimethyl ammonium chloride
- Lauryl dimethylbenzyl chloride
- Lauryl trimethyl ammonium bromide or dodecyl trimethyl ammonium bromide
- Myristalkonium chloride or miristalkonium chloride
- Myristalkonium chloride or miristalkonium chloride
- Myristyl trimethyl ammonium bromide or tetradecyl trimethyl ammonium bromide
- N-Stearylstearamide/Cocotrimethylammonium chloride
- Stearyl dimethylbenzyl ammonium chloride
- Stearyl trimethyl ammonium bromide or octadecyl trimethyl ammonium bromide
- Stearyl trimethyl ammonium chloride or octadecyl trimethyl ammonium chloride
- Tallowtrimethyl ammonium chloride
- Trimethylsoya alkyl, chlorides

associated with the product. As new QAC chemicals are found they can be added to this list for a quick comparison.

METHODOLOGY

Table 3 shows several recommendations for evaluation of a product that is suspected to contain QAC. Typically the product MSDS sheets will be evaluated early in the study because of their availability. When talking to the manufacturer of the product simply ask if it contains any QAC without outlining that the reason for your interest is a problem of inhibition in the wastewater treatment plant.

Table 3. Approach to Evaluate If a Product Contains QAC

- Internet searches for the product
- Web site of the manufacturer of the product
- Product MSDS
- Examine the product label
- Phone call to manufacturer's technical department

Discovery That QAC Inhibits Nitrification

Smith & Loveless manufactures and sells package wastewater treatment plants throughout the United States and the world. Many of our plants have been designed to meet low nitrogen limits due to the needs of a specific area of the country. Several years ago we discovered that there were a few designs that did not nitrify as low as expected and yet their design and application were similar to designs in other locations that had been proven to successfully nitrify to very low levels. Discussions with Dr. Jim Young found a possible reason why some plants did not nitrify and others easily nitrified. Dr. Young had published a paper that examined numerous possible chemicals that could have detrimental effects on biological wastewater treatment processes (2001). QAC was one of the compounds that stood out as a key problem in nitrification; it was found that nitrification was completely inhibited at a concentration of 2 mg/L or less. Extensive searches have not found any other papers or research on QAC effects on wastewater processes; however, we began to test for QAC at some plants that were having difficulty in nitrifying.

QAC Identification Problems

Analytical measurement of QAC is not widely available at the relatively low concentrations of concern to nitrification inhibition. It is not possible, as some might think, to detect that QAC is present in a wastewater by testing for nitrogen expecting the nitrogen to be much higher than normal. The amount of nitrogen in a solution of QAC will usually be less than 2 or 3 % because of the number of long chain radicals in QAC. Each of the four radicals attached to one nitrogen atom will have 12 to 18 carbon atoms. If each radical has 16 carbon atoms the weight of the carbon atoms alone is 768 grams compared to the molecular weight of nitrogen which is 14 grams. The nitrogen would be 1.8% of the weight of just the nitrogen and carbon alone. There will always be other atoms such as chlorine and bromine in the makeup of the QAC. Thus, the percentage of nitrogen in a QAC product will typically be less than 1% of the QAC. If the QAC were 10 mg/L in the wastewater, then the amount of nitrogen associated with the QAC would be 0.1 mg/L.

Overdosing of QAC is a frequent problem that often results in higher than necessary QAC in a wastewater. Human nature often causes an even higher dose of QAC to be used than is recommended because “if a little QAC will work, then a lot more is even better.” It is important, that users of QAC not use more than is recommended on the product’s container.

Analytical methods are available for testing high concentrations, however, these analytical methods will not detect the low QAC concentrations of 0.5 to 10 mg/L needed to evaluate raw wastewater for nitrification inhibition. Currently the best method found for testing samples with low to moderate concentrations of QAC is a colorimetric method sold by the HACH Company.

Another problem with identifying the presence of QAC is that it is typically discharged into the sewer in slugs. For example, a counter top may be sprayed down with a disinfectant containing QAC to sterilize the counter top. It is typical to apply a disinfectant sufficient to achieve 400 to 500 parts per million QAC on the counter top to obtain a good bacterial kill. After allowing a sufficient time for the disinfectant to work, the counter top is flushed off with water and discharged into the sewer. The end result is that a slug of QAC enters the wastewater treatment plant at a concentration that completely inhibit nitrification. A few hours before the QAC discharge and a few hours following the QAC discharge, no QAC may be found when samples are taken because the QAC slug has passed. However, the slug of QAC has a rapid effect on the nitrifying bacteria and stops nitrification for a week or two. This demonstrates the difficulty in sampling for the presence of QAC in a wastewater.

If sufficient time occurs between QAC slugs, nitrification may be reestablished between QAC discharges and the operator is even more confused because the plant sometimes nitrifies completely and some times it does not nitrify at all. BOD and TSS removal is seldom affected by QAC. If QAC is discharged once a week, it is highly probable that nitrification will be prevented for a continuous period of time.

Because of the nature of QAC discharges, sampling for QAC is often difficult and the results usually indicate low or no QAC present. Yet in fact, nitrification is being inhibited and QAC is responsible because the major concentration of QAC was not detected. When 0.5 to 1.0 mg/L or more QAC is found in a wastewater that is not nitrifying (assuming the design and operation are good), it can be assumed that QAC is causing poor nitrification. A more extensive sampling program may be required.

It is frequently useful to check hotels, laundries, and other major industries MSDS sheets to determine if there are any major chemicals containing QAC being used. A check of the products used by grocery stores, butcher shops, schools, and pharmaceutical manufacturers can also be useful because of their frequent use of QAC products. However, the MSDS sheets do not always show the presence of QAC since QAC is considered to be non toxic.

Symptoms of the Presence of QAC

The symptoms of a treatment plant with high QAC in the influent is that BOD and TSS removal is usually good; however, high concentrations of ammonia are present in the effluent. The effluent will frequently indicate a relatively high concentration of organic nitrogen. Due to

interferences that sometimes occur in the analytical procedures for ammonia and TKN, ammonia may have a higher concentration than TKN. The heterotrophic bacteria that remove BOD are usually not inhibited or significantly affected by the QAC. As a matter of fact, the QAC will be slowly degraded by the same bacteria that remove BOD. The problem is that the rate of removal of the QAC is very slow.

RESULTS AND DISCUSSION

Prevent Nitrification Inhibition due to QAC

Solutions to preventing inhibition of nitrification due to QAC are relatively simple but usually not without significant costs. The first and best approach is to remove the products containing QAC to prevent the inhibition of nitrification at the wastewater treatment plant. If it is not feasible to exchange QAC products with products without QAC then it will be important to provide the optimum conditions needed to treat the QAC so nitrification inhibition will not occur. There are four options that have been found by experience or observation that can reduce the inhibition effects sufficiently so nitrification can be achieved. They are as follows: add a large aerated equalization zone ahead of the treatment plant, reconfigure the existing plant for optimum QAC removal, increase the size of the existing biological aeration zone, and add a post aeration zone following the existing treatment plant. In each situation where QAC inhibits nitrification, it is necessary to provide a longer hydraulic retention time than normal which amounts to reducing the organic loading on the treatment system. This is due to the slow biodegradation of QAC.

1. Removal of QAC Products

A dog training facility was using a QAC disinfectant to clean their dog runs and prevent disease among the dogs. Their treatment plant was designed to remove nitrogen, however the effluent ammonia was consistently high. The owners did not want to change from the QAC disinfectant for fear the dogs might spread some disease. However the owner finally did change their disinfectant. Figure 2 shows two years of influent nitrogen data from this dog training facility. The influent nitrogen measured from slightly more than 30 mg/L nitrogen to over 90 mg/L nitrogen. This was typical of the influent since the treatment plant was started up. Figure 3 shows the effluent ammonia for the same two-year period. Figure 3 shows the effluent ammonia ranging from about 6 mg/L to almost 40 mg/L ammonia until the first of 1995 where suddenly the effluent ammonia dropped to very low levels. The drop in effluent ammonia occurred shortly after a chlorine type disinfectant was used to replace the QAC disinfectant. This drop in ammonia occurred because nitrification was no longer inhibited by QAC.

2. Large Aerated Equalization Addition

Smith & Loveless had provided a fixed film process called the FAST[®] process to a school in the New England area. The school wastewater had very high nitrogen concentration and a relative low BOD. Discharge limits were met during the first few years of operation but then the effluent nitrogen began to exceed the discharge limits. Sampling was conducted without determining the

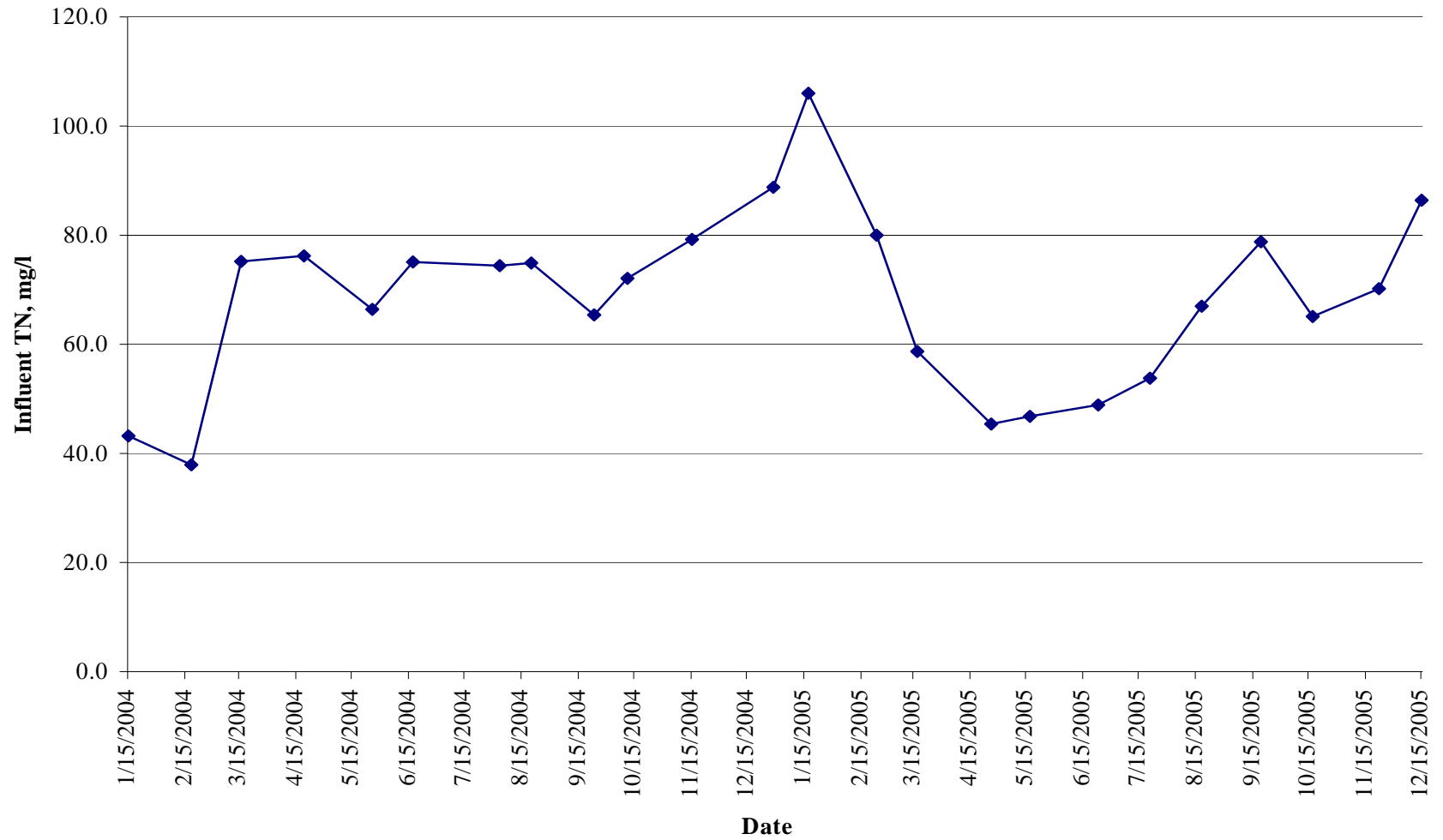


Figure 2. Dog Training Facility Influent Total Nitrogen

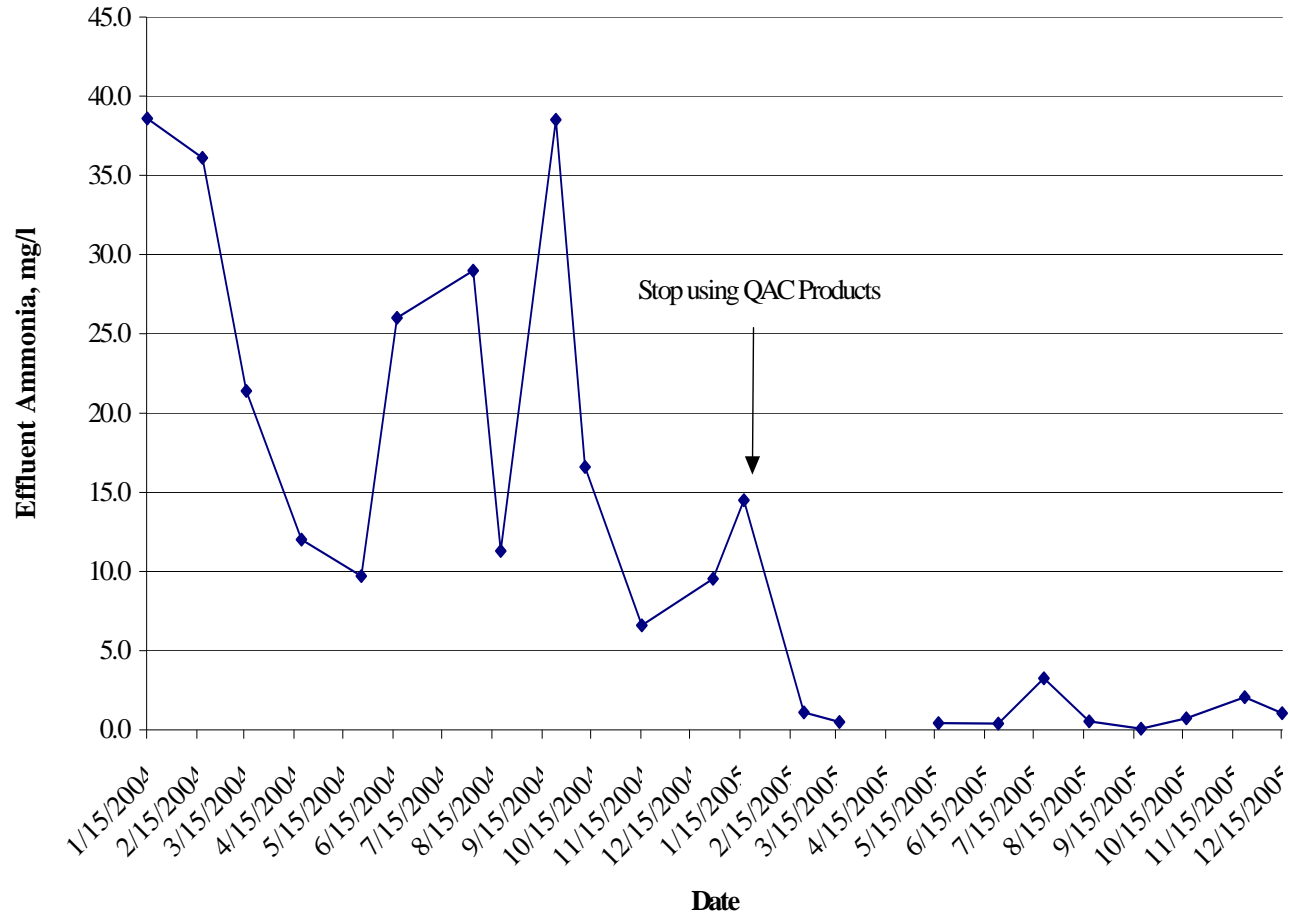


Figure 3. Dog Training Facility Effluent Ammonia

problem. It was decided to test for QAC after becoming aware of Dr. Jim Young’s paper. Table 4 shows the QAC data varied from 1 mg/L to 4.4 mg/L prior to the addition of the aerated equalization tank. The QAC shown on Table 4 also shows that the school has significantly reduced the use of QAC products, but not completely. This reduction was achieved by review of the MSDS sheets for all products used in the school. There were several products found that contained QAC but it was difficult for the school to remove all the QAC from their wastewater. Therefore another approach was needed.

Table 4. QAC Data for Addition of Aerated Equalization Zone

Date	Quaternary Ammonia Compounds		Aerated Equalization mg/l
	Raw Waste mg/l	Septic Tank mg/l	
Sep 20-21, 2001	2.52		NA
Oct 25-26, 2001	4.4		NA
Nov 20-21, 2001	3.07		NA
Dec 17-18, 2001		1.2	NA
Jan 22-23, 2002	2	1.9	NA
Feb 11-12, 2002	2.5	4.2	NA
Mar 25-26, 2002	<1	<1	NA
Apr 29-30, 2002	2.37	1.2	NA
Data After Addition of Aerated Equalization Tank			
May 14-15, 2006	< 1	(1)	< 1
Jul 20-21, 2006	1.9		2.7
Aug 21-22, 2006	< 1		< 1
Sep 21-22, 2006	< 1		< 1
Jan 15-16, 2007	< 1		< 1
Mar 27-28, 2007	< 1		< 1
Apr 25-26, 2007	3.6		< 1
Jun 12-13, 2007	1.2		< 1
Jul 30-31, 2007	< 1		< 1
Aug 20-21, 2007	1.2		< 1
Sep 25-26, 2007	< 1		< 1
Oct 24-25, 2007	1.6		1.9
Nov 13-14, 2007			

(1) QAC data not taken in septic tank after addition of aerated equalization tank.

Several treatment alternatives were evaluated so the nitrogen limits could be met. The two most promising treatment options were to add an additional **FAST**[®] unit, or add a large equalization zone ahead of the existing treatment system. The addition of the equalization was selected due to a lower capital cost and ease of implementation into the existing treatment plant. The equalization tank was designed for a minimum two hours hydraulic retention time and had facilities to recycle solids from the existing **FAST**[®] system to the equalization tank. The

equalization tank was aerated at a rate about three times the normal aeration rate for an equalization tank. The high rate of aeration was necessary to provide air to aerate the raw wastewater as well as for the bacteria to metabolize the QAC. Figure 4 shows the effect of before and after adding the aerated equalization. The plant went from essentially no nitrification to almost complete nitrification after the addition of the aerated equalization tank. Figure 5 shows the effluent total nitrogen was typically less than 5 mg/L and always less than 10 mg/L effluent nitrogen. The QAC was sufficiently metabolized to stop inhibition by QAC with the addition of an aerated equalization tank.

3. Reconfiguration of Existing Treatment System

At another school an existing treatment system was unable to meet its discharge limits. The influent nitrogen ranged from 20 to 93 mg/L with an average value of 65 mg/L. The influent BOD averaged 81 mg/L for the same period. For this plant there was partial nitrification and the effluent averaged 34 mg/l nitrate as N. The original configuration for this plant had a two stage settling tank followed by two parallel aeration tanks, followed by an anoxic tank with a methanol feed system, and finally a re-aeration tank. Because nitrification is a rate dependent process, it was decided to put the two aeration tanks in series. This would allow the BOD reduction to occur first with nitrification to follow in the rest of the aeration. Because the BOD removal is much more rapid than nitrification, the two unit processes proceed in sequence, with BOD removed first and then nitrification. Figure 6 shows the success of this modification with low total nitrogen in the effluent that easily met the discharge limits.

4. Increase Size of Existing Biological Aeration Zone

The rate of biodegradation of QAC is slow; however, one way to address QAC compounds is to reduce the QAC below the level that inhibits nitrification. The main problem in designing either a new treatment system or a modification to an existing treatment system is that the rate of metabolism of QAC is unknown. This is an area that needs extensive research study. Research may show that different types of treatment systems will require different loading rates for effectively preventing nitrification inhibition.

5. Post Aeration Treatment

A fixed film treatment system was not able to meet the nitrogen discharge limits due to high QAC in the wastewater. The operator decided to try adding an aeration tank containing additional media following the existing system. The media was used to provide a large surface area for bacterial growth and thus increase the amount of bacteria for nitrification. When this aeration tank was put into operation nitrification was achieved and the plant met its discharge limit. It appears that the QAC was oxidized below inhibition levels in the existing treatment plant; however there was not enough treatment capacity left to nitrify. The aeration tank provided the additional treatment capacity to finish the needed nitrification and meet the discharge limits. While this was a trial without a well defined design it shows that effective treatment can be achieved with additional aeration using a fixed media polishing system.

CONCLUSIONS:

1. QAC will inhibit nitrification at 2 mg/L or less concentrations
2. QAC does not inhibit BOD removal
3. QAC is biodegraded at a slow rate
4. Removal of products containing QAC is the best approach to stop nitrification inhibition
5. Different treatment modifications can reduce QAC so nitrification is not inhibited
6. Additional research is needed to quantify QAC biodegradation and to provide a more accurate approach to design of treatment facilities to prevent nitrification inhibition

REFERENCES

Young, James C. (2001) *Impact of Cleaning and Disinfecting Agents on Biological Treatment Processes*, Industrial Waste Technical Conference, Charleston, SC.

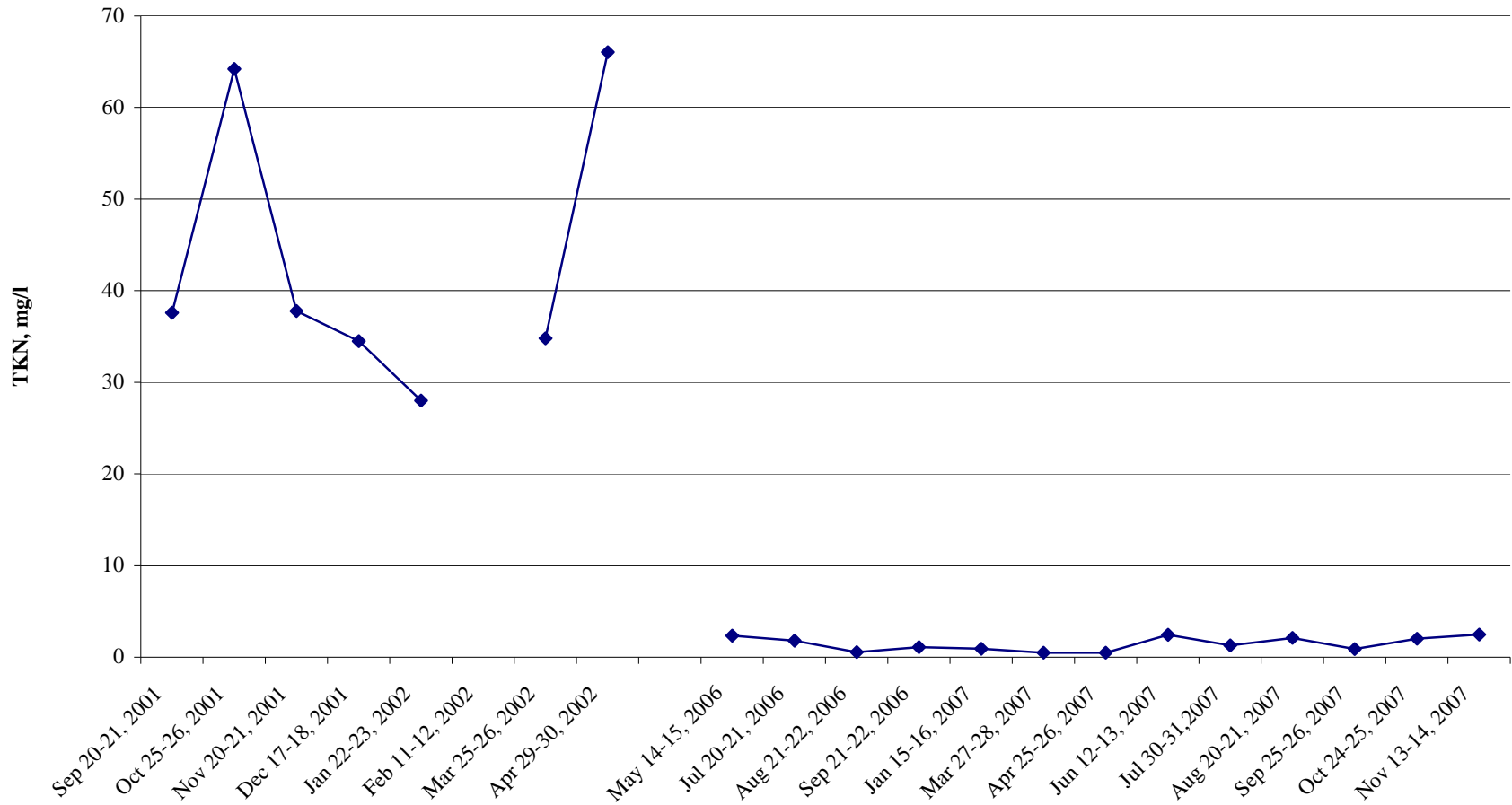


Figure 4. Before and After Addition of Aerated Equalization

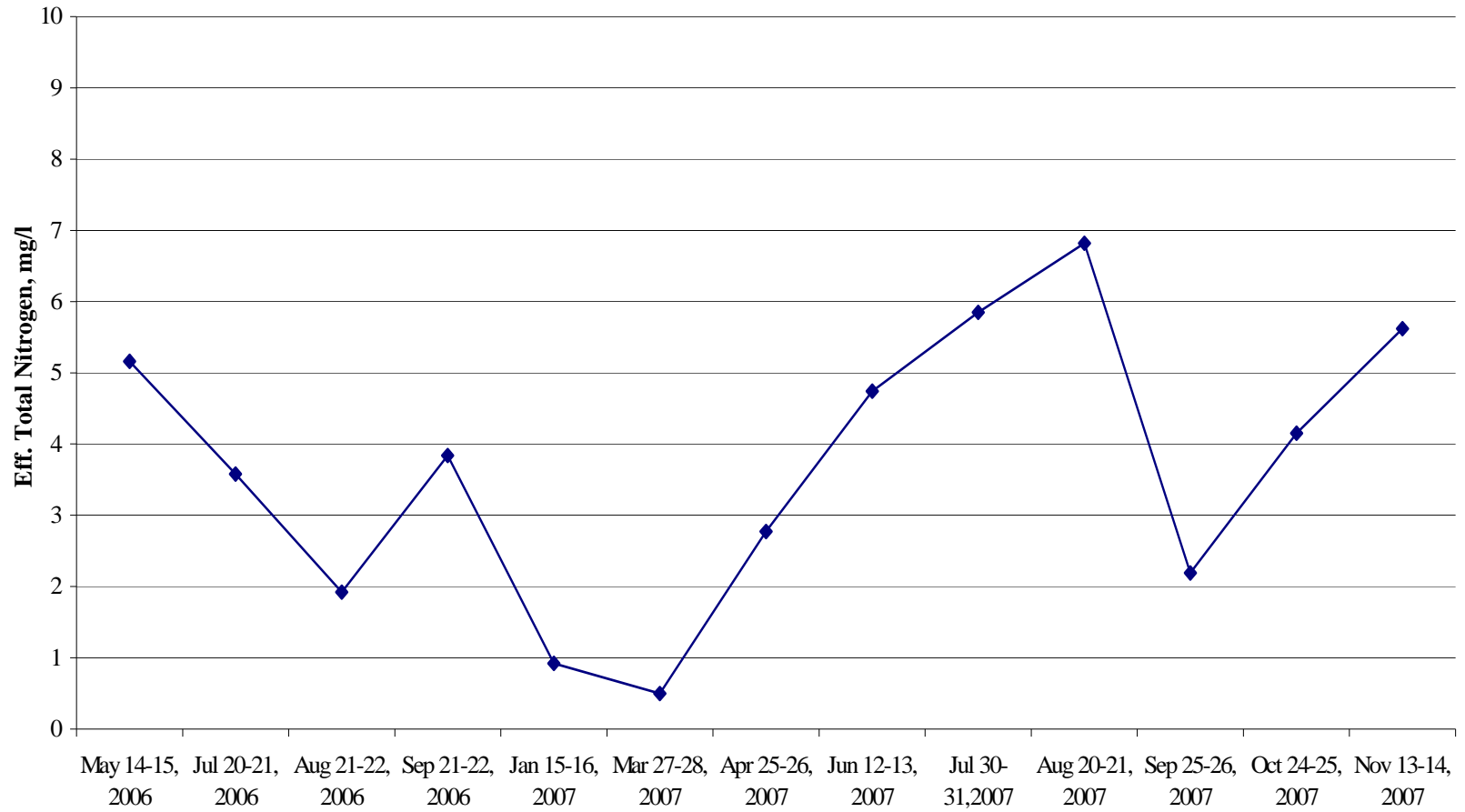


Figure 5. Effluent Nitrogen After Addition of Aerated Equalization

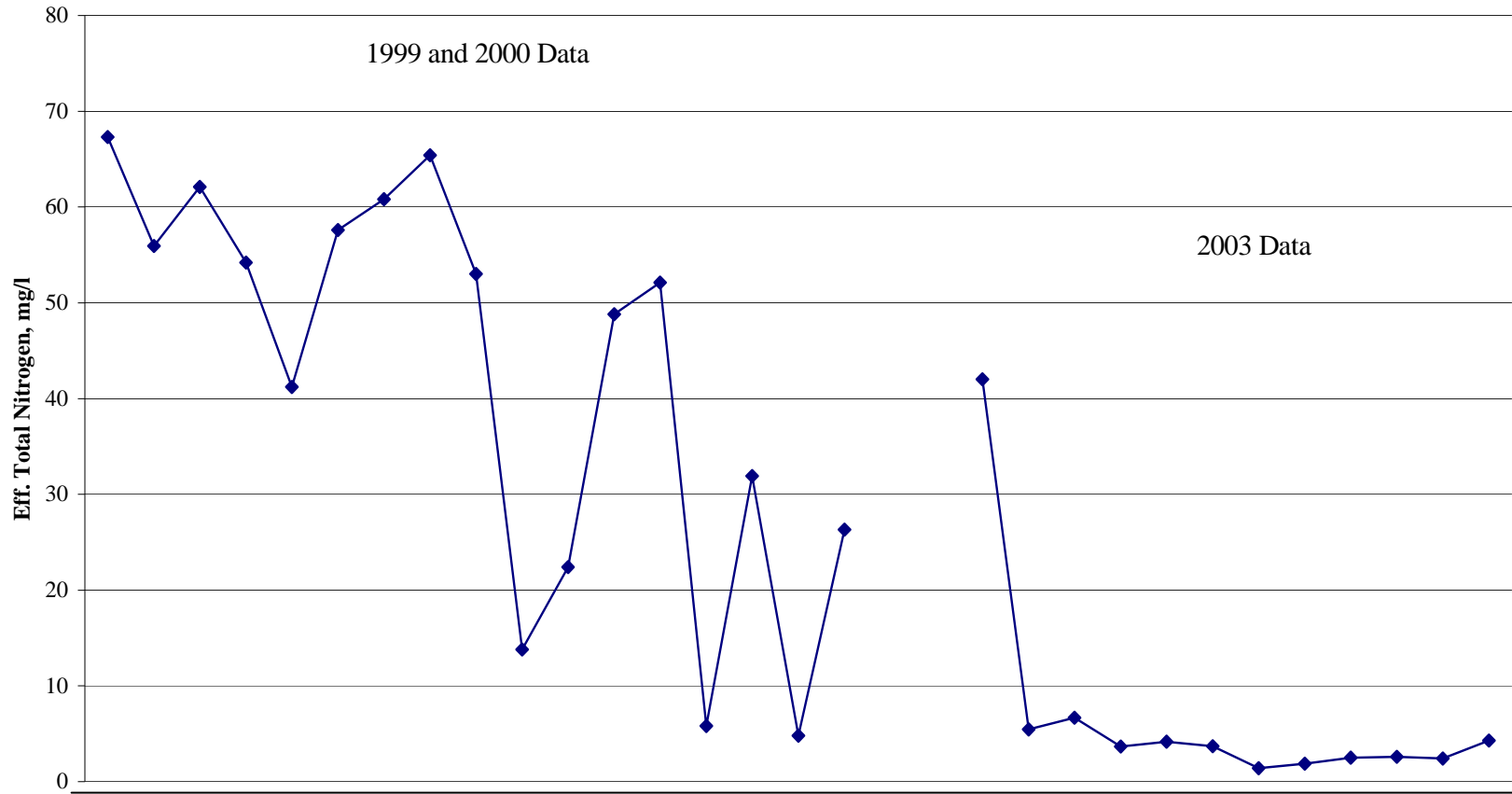


Figure 6. Before and After Reconfiguration of Plant