



Keys to Better Nitrification

Incomplete reactions can lead to nitrite lock

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When the nitrification process is controlled properly, nitrite-nitrogen seldom exceeds 1.0 mg/L. As soon as ammonia is oxidized to nitrite by ammonia-oxidizing bacteria (AOB), the nitrite is oxidized to nitrate by nitrite-oxidizing bacteria (NOB).

Nitrite will increase, however, under certain environmental conditions, such as a poorly established or inhibited NOB population. The NOB population may be poorly established during nitrification startup or inhibited because of environmental conditions — some of which operators can control.

Following are some of the causes and effects of nitrite lock.

Effects of Nitrite Lock

Nitrite lock can result in poor disinfection, effluent violations, and toxicity.

Nitrite-chlorine reactions. The most frequent concern about nitrite lock is the chemical reaction between chlorine and nitrite, and the subsequent effect on disinfection. Nitrite reacts with elemental chlorine as follows:



Nitrite reacts with sodium hypochlorite as follows:



Typically, 1 mg/L of nitrite-nitrogen will react with (consume) 5 mg/L of free chlorine. Chlorine-nitrite reactions can result in poor disinfection, increased chlorine costs, and possible pH violations.

Although free chlorine reacts readily with nitrite, chloramines do not. Some of the facilities that know this have modified their seasonal startup strategies to avoid nitrite lock or added other sources of ammonia (such as ammonium hydroxide or anaerobic digester centrate) to control the effect of nitrite lock on chlorination.

Nitrite toxicity. The U.S. Environmental Protection Agency (EPA) has determined that keeping receiving water concentrations of nitrite-nitrogen below 5.0 and 0.06 mg/L will protect warm-water fish and salmonid species, respectively. However, regulators have not set water quality criteria for nitrite, because they believe the nitrite-nitrogen concentrations "that would exhibit toxic effects on warm- or cold-water fish could rarely exist in nature," according to EPA.

However, while such concentrations might rarely occur in nature, they can exist in wastewater

treatment plant effluent during nitrite lock. If an effluent sample contained these levels of nitrite-nitrogen during whole effluent toxicity testing, it could fail the test.

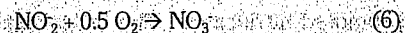
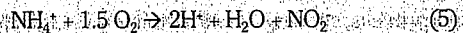
Denitrification. Denitrifying organisms use nitrate as a terminal electron acceptor when oxidizing organic compounds, reducing nitrate to nitrogen gas. Nitrite can be either an intermediary ion or a terminal electron acceptor in this process. In fact, denitrification may be faster when the organism uses nitrite rather than nitrate.

The most significant effect of nitrite lock on denitrification would be floating solids in the secondary clarifiers and subsequent solids loss.

Key Nitrification Relationships

Understanding the causes and potential effects of nitrite lock requires a fundamental knowledge of the relationships between AOB and NOB, as discussed below.

The stoichiometric equations for oxidizing ammonia to nitrite (Equation 5) and oxidizing nitrite to nitrate (Equation 6) are as follows:



These equations show that 7.1 mg/L of alkalinity is consumed during nitrification. AOB consume all the alkalinity. In low-alkalinity wastewaters, AOB can consume enough alkalinity to lower the pH to levels that can inhibit NOB.

Equations 5 and 6 also show that AOB and NOB are obligate aerobes. AOB consume about 3.43 mg/L of oxygen for each 1 mg/L of ammonia-nitrogen oxidized to nitrite-nitrogen. NOB consume about 1.14 mg/L of oxygen for each 1 mg/L of nitrite-nitrogen oxidized to nitrate-nitrogen.

Nitrite lock can occur when NOB populations are fully established, suggesting that NOB are more sensitive to environmental factors. According to Barnard (1994), *Nitrobacter* species are more vulnerable "to toxic or other influences and would be the first to suffer as a result to any disturbance to the environment ... a dissolved oxygen (DO) level which is too low, a pH value which is too high or too low, or the influence of toxic inhibitors."

NOB grow faster than AOB. As soon as AOB produce nitrite, a well-established NOB population will assimilate it and convert it to nitrate. When the temperature is above 27°C, AOB grow faster than NOB, potentially resulting in an increase in the nitrite concentration.

Although NOB grow faster when the temperature is below 27°C, the NOB population will lag behind the AOB population during startup because NOB need nitrite as an energy source.

These relationships show that a range of environmental conditions could cause nitrite lock, including low DO, alkalinity, or pH; high temperature or pH; and toxic or inhibitory substances. Nitrite lock also may occur during startup or seasonal startup of nitrification facilities, because NOB grow more slowly than AOB.

Common Troubleshooting Mistakes

Nitrite lock is often prolonged by limited data and a poor understanding of process relationships. Four common practices limit troubleshooting and timely corrective actions.

Combined nitrite-nitrogen and nitrate-nitrogen analyses. Many discharge permits express oxidized nitrogen analytical requirements as the sum of nitrite-nitrogen and nitrate-nitrogen concentrations. So, it is not uncommon for treatment plant staff to use an analytical procedure that combines the measurements and fails to distinguish nitrite-nitrogen from nitrate-nitrogen.

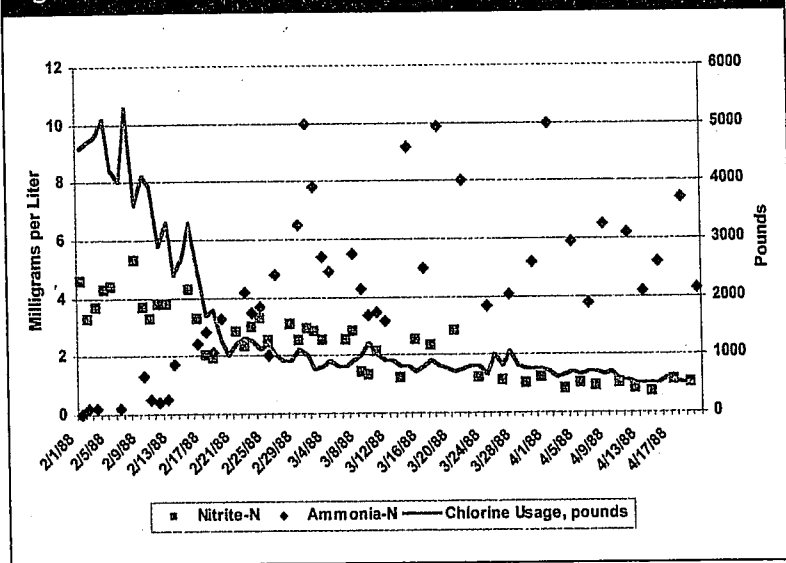
Evaluations based on final effluent parameters. Many of the analytical parameters for evaluating nitrite lock — including nitrite concentration, alkalinity, and pH — are affected by chlorine disinfection. So, facilities that use chlorine disinfection cannot use final effluent data to effectively evaluate the causes of nitrite lock. They should use secondary effluent data instead.

Assumption that NOB can only be inhibited by external sources. NOB can be inhibited by both external sources (such as toxic or inhibitory discharges) and wastewater characteristics (such as low temperature) that are beyond an operator's control. NOB also can be inhibited by internal sources, including

- chlorine used for filamentous control, secondary clarifier chlorination rings, and filter backwashing;
- low pH because of nitrification in low-alkalinity wastewaters (if the wastewater contains less than 150 mg/L of alkalinity as calcium carbonate, AOB can consume enough to drop the pH and inhibit NOB); and
- low DO in the biological process (which also can inhibit AOB).

Slow response. Nitrifying organisms are a small percentage of the mass in a biological treatment system. If the cause of nitrite lock is not determined quickly, NOB can be wasted from the secondary process. Then, more time will be needed to re-establish the NOB population.

Figure 1. Chlorine Consumption During Nitrite Lock



Case Studies

The following examples illustrate various causes and effects of nitrite lock that wastewater treatment professionals have learned during 19 years of experience. The first two case studies are based on forensic analyses of historical data; the other two were assessed when the nitrite lock occurred.

Salem, Ore. In 1988, the Willow Lake Wastewater Treatment Plant in Salem, Ore., switched its activated sludge process from pure oxygen to diffused air and converted it to operate in series with the trickling filter rather than in parallel. The newly combined trickling filter-activated sludge (TF/AS) process had nitrite lock for about 2 weeks during startup.

Historical data show that the secondary effluent contained 4 to 5 mg/L of nitrite-nitrogen, requiring the addition of up to 10 times more chlorine than normal (see Figure 1, above). The reactions between nitrite and chlorine consumed the chlorine and resulted in poor disinfection and higher operating costs. The data also show that chlorine use decreased as the ammonia-nitrogen levels in secondary effluent increased (because chloramines do not readily react with nitrites).

In addition, when the activated sludge basin was converted from pure oxygen to fine-pore air diffusion, the pH of the

mixed liquor suspended solids (MLSS) rose from about 6.2 to 6.5. The pure oxygen system was converted to air 2 days before the activated sludge process was started up and continued to operate in parallel with the trickling filter until full TF/AS operations began. When covered, pure oxygen basins typically have lower pH than air-activated sludge because of the high partial pressure of carbon dioxide in the headspace.

Once the TF/AS

process was brought on-line, nitrification increased in the secondary process even though MLSS and DO concentrations steadily declined. Nitrification began to decrease about Feb. 12. The trickling filter's load had doubled when the plant switched over to the TF/AS process, seeding the air-activated sludge process with nitrifiers. High MLSS and DO concentrations promoted nitrification. The data suggest that DO was the key limiting factor, because the MLSS concentration increased dramatically on Feb. 17 with no corresponding change in nitrification.

As the MLSS's pH increased during the 2-month period, the nitrite-nitrogen concentration decreased (see Figure 2, below). The increasing pH correlated to the decreasing nitrite concentration, suggesting that nitrite lock was caused by low pH (particularly below 6.7).

Figure 2. Secondary Effluent Nitrite-Nitrogen and pH Comparison

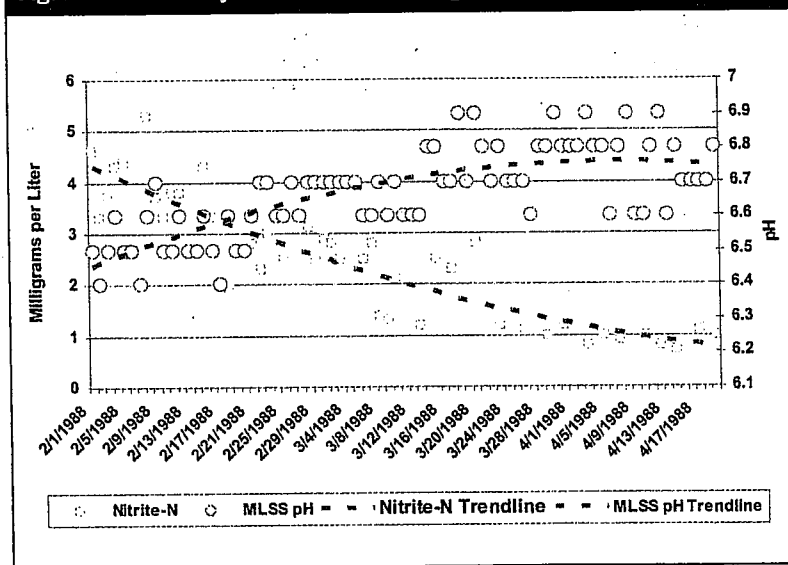
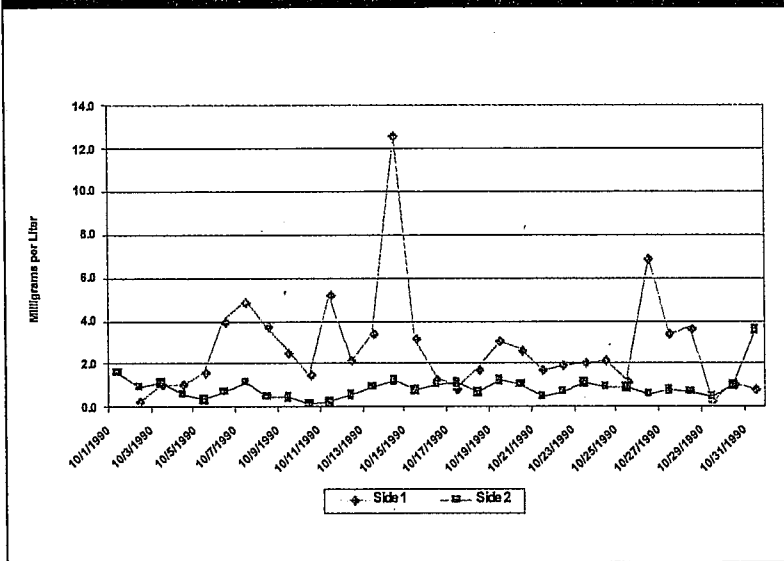


Figure 3. Secondary Effluent Nitrite-Nitrogen



Troubleshooters initially suspected that the cause was the low alkalinity's effect on pH, until both sides had similar nitrification rates and alkalinity levels at the end of the month. Effluent nitrite levels remained basically stable in side 2 but continued to fluctuate in side 1. Also, the MLSS's pH on side 1 ranged from 6.7 to 7.2 (only one data point was below 6.8), which should not inhibit NOB. So, the nitrite lock was not caused by low pH.

Also, Willow Lake's influent alkalinity was low (130 to 150 mg/L). When the process was completely nitrifying, AOB consumed enough alkalinity to lower the MLSS's pH and thereby inhibit NOB. Because the facility was neither required nor designed to nitrify, no additional alkalinity was available.

This example demonstrates two important aspects of nitrite lock:

- Low pH can inhibit NOB.
- Chloramines do not readily react with nitrite.

Durham, Ore. In October 1990, nitrite lock occurred intermittently in a secondary treatment train at the Durham (Ore.) Wastewater Treatment Plant (owned by Clean Water Services, formerly the Unified Sewerage Agency). At the time, the plant had two parallel — but independent — secondary treatment trains. At first, side 1 was carrying about 15% more biological mass than side 2, resulting in a higher, yet inconsistent, nitrification rate. About midmonth, side 2's mass began to increase, as did its nitrification rate.

Interestingly, side 1's effluent nitrite-nitrogen levels fluctuated significantly, while side 2's effluent nitrite-nitrogen levels remained fairly stable, even when its nitrification rate rose (see Figure 3, above). This discrepancy suggested that side 1's nitrite lock was caused by something specific to the treatment train.

Troubleshooters eventually determined that the most likely cause was low DO. According to a monthly process summary memorandum (Unified Sewerage Agency, 1990), "The aeration basin dissolved oxygen problems gradually were fixed during the month. The system is now back to normal. ... Early in the month, microscopic examination revealed that Side 2 looked very healthy, but Side 1 was lousy. As the aeration system problems, which mainly affected Side 1, were fixed, Side 1 bugs gradually improved during the month."

This example illustrates that nitrite lock can be induced by process-specific variables. NOB and AOB require oxygen to thrive.

Las Vegas. In December 1994, nitrite lock occurred during the startup of a nitrification system at the City of Las Vegas Water Pollution Control Facility. Effluent

Figure 4. Progression of Nitrification During Startup

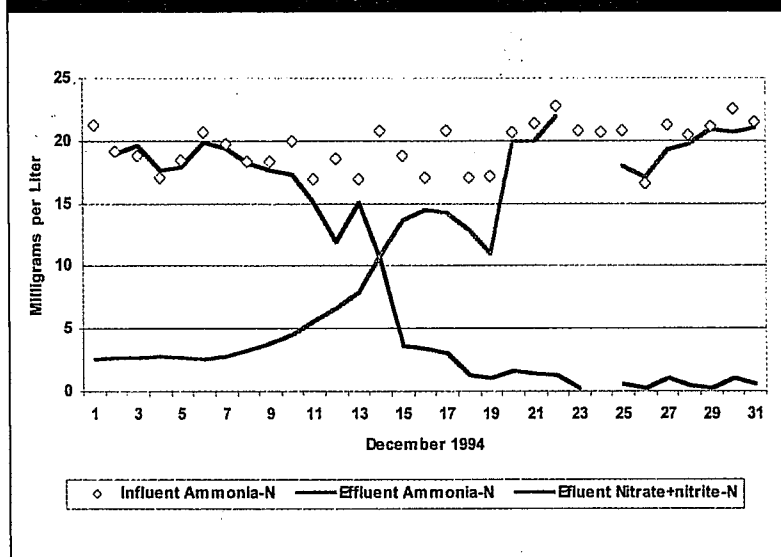
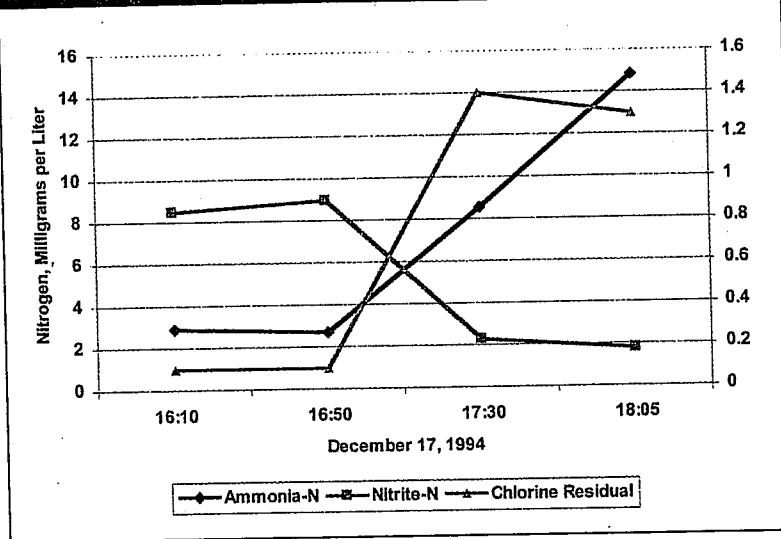


Figure 5. Effect of Increasing Ammonia Concentration To Regain Chlorine Residual



ammonia concentrations were decreasing, the combined effluent nitrite and nitrate concentration was increasing, and disinfection effectiveness was lost (see Figure 4, p. 85). Effluent fecal coliform concentrations began to increase significantly on Dec. 14.

On Dec. 16, lab analysis confirmed that nitrite lock was occurring. Comparisons of prechlorination nitrite concentrations with post-chlorination chlorine residual showed that chlorine was reacting with nitrite.

Because chloramines do not react readily with nitrite, troubleshooters mixed a non-nitrified effluent with the nitrite-laden one. Raising the ammonia concentration above the nitrite concentration quickly produced a measurable chlorine residual (see Figure 5, above), but this solution was unsustainable because of hydraulic constraints. Fortunately, the NOB population was large enough by Dec. 24 to oxidize the nitrite to nitrate for effective disinfection.

This example illustrates three important aspects of nitrite lock:

- Nitrite lock can occur during the startup of a nitrification process.
- Nitrite-nitrogen and nitrate-nitrogen should be analyzed separately.
- Chloramines can significantly reduce

the chlorine demand associated with nitrite lock.

El Paso, Texas. In 1999, an air-activated sludge process that could provide full nitrification began operating at the Haskell R. Street Wastewater Treatment Plant, which is owned by El Paso Water Utilities (EPWU). Nitrite lock was expected during startup, so the project team developed a strategy to minimize it. The strategy involved increasing MLSS slowly to ensure that the ammonia-nitrogen

concentration always exceeded the nitrite-nitrogen concentration in secondary effluent.

Nevertheless, the first two attempts resulted in nitrite lock. The team suspected toxic inhibition was causing the problem, because the process variables were within nitrification ranges.

Unlike most facilities, the EPWU plant's discharge permit required a minimum chlorine residual of 1.0 mg/L, so it used more chlorine than would be expected. Nitrite lock further increased chlorine demand, straining the chlorination system until it could not supply enough chemical to the chlorine contact tank to meet demand and maintain the required residual. Adding calcium hypochlorite only helped somewhat, so the team tried intermittently adding chlorine solution to one of the secondary clarifier's weir chlorination rings.

Figure 6. Secondary Effluent Ammonia-Nitrogen and Nitrite-Nitrogen

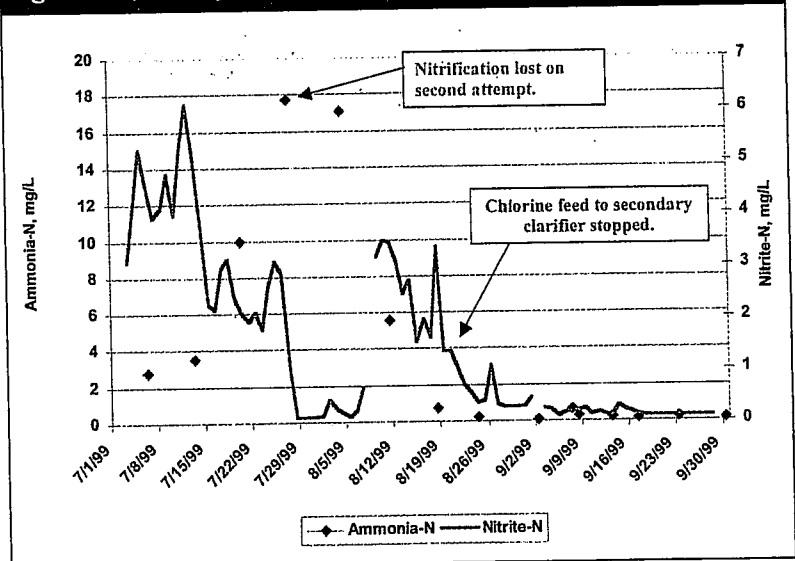
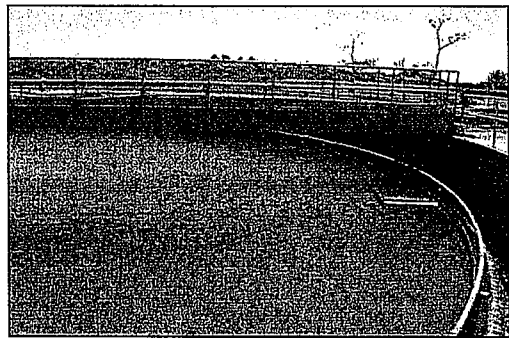
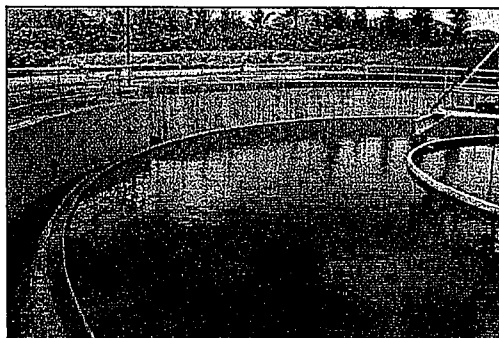


Figure 7. Coloration-Associated Chlorine-Nitrite Reactions



Clarifier 1



Clarifier 2

The water in that clarifier turned green on Aug. 20. The team measured the clarifier's chlorine residual and found that concentrations were as high as 3.5 mg/L. So, the team immediately stopped adding chlorine to the weir chlorination ring. Within a week, full nitrification was achieved. The team suspected that the chlorine had inhibited NOB in the clarifier's sludge blanket. When chlorine feed to the chlorination rings was stopped, the third attempt to achieve nitrification was successful (see Figure 6, p. 86).

This example illustrates how onsite sources of toxicity can cause nitrite lock. In this case, toxic concentrations of chlorine were being introduced to the return activated sludge, thereby inhibiting NOB.

Useful Observation

The observation that nitrite-chlorine reactions turned the EPWU plant's water green was useful less than 2 weeks later at a wastewater treatment plant in Hawaii. The Hawaii plant has two secondary clarifiers that operate in parallel (see Figure 7, above); both are fed mixed liquor from one aeration basin. Both clarifiers were producing excellent effluent with little turbidity, but clarifier 1's water was green, while clarifier 2's was not.

An analysis of the MLSS indicated that nitrites were present (concentrations were not quantified). Both clarifiers have chlorination rings around the weirs that are used to inject chlorine into the water for disinfection. Clarifier 1's chlorine ring is above the water surface and injects chlorine down into the water via multiple points. Clarifier 2's chlorine ring is just below the water surface, and the chlorine is injected laterally against the clarifier wall.

Discussions with plant staff indicated that clarifier 1 turned green shortly after scale buildup was removed from the chlorine ring's nozzles. The team suspected that removing the scale allowed most — if not all — of the chlorine feed to be directed to clarifier 1. The team also suspected that chlorine was

inhibiting NOB in clarifier 1's sludge blanket, just as it had at the EPWU plant.

When the chlorine was shifted from the clarifier chlorine rings to an effluent junction box, the green color appeared immediately at the junction box and disappeared from clarifier 1 within 24 hours. Within a week, full nitrification was achieved.

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For More Information

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