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CONTROLLING NITRATE CONCENTRATIONS IN LARGE SEAWATER FACILITIES

Curators of large aquaria where there is no significant primary production and water changes are impractical have been using biological denitrification to control high nitrate concentrations. The two denitrification systems described in this study operate in different ways: the Living Seas uses a batch system, while the New Jersey State Aquarium uses a flow-through system. The rate of denitrification controls the operation of the Living Seas system, while water residence time controls the operation of the New Jersey State Aquarium system.

Key Words: nitrate, denitrification, seawater aquaria, modeling

1. INTRODUCTION

One of the most difficult challenges in seawater aquarium and mariculture industry is the control of high nitrate concentrations. Many of the facilities host primarily heterotrophic organisms and their seawater exhibits increasing nitrate concentrations over time. Nitrate in these systems is primarily produced by bacteriological nitrification of excreted ammonium nitrogen (Strotmann and Windecker, 1997), although other processes (e.g. disinfection by ozone) can provide additional oxidation pathways from ammonium to nitrate (Honn and Chavin, 1976).

Many small aquarium and mariculture facilities control high nitrate concentrations by performing regular water changes. In a very large system, this is impractical for two reasons: (1) the size of the tank makes it operationally difficult to replace a significant fraction of water, and (2) the expense of preparing large volumes of artificial seawater for facilities located far from the ocean can be prohibitive (Grguric, 1990). As a result of these considerations, biological denitrification has been selected as a method of choice for controlling nitrate concentrations in several large seawater aquaria. The process consists of adding organic carbon to seawater and employing facultative anaerobic bacteria (usually Pseudomonas family) to consume nitrate in seawater. Under anaerobic conditions, these bacteria use nitrate as an oxidizing agent for organic carbon. Methanol is commonly used as a source of organic carbon, due to

its relatively low cost and low sludge production compared with other organic compounds (Timmermans and Van Haute, 1983; Koch and Siegrist, 1997). Through consecutive redox reactions (equations 1, 2), nitrate is first reduced to nitrite and then to nitrogen gas (Jeris and Owens, 1975).

(1) $3\ NO_3^- + CH_3OH \longrightarrow 3\ NO_2^- + CO_2 + 2\ H_2O$

(2) $2\ NO_2^- + CH_3OH \longrightarrow N_2 + CO_2 + H_2O + 2\ OH^-$

The net denitrification reaction is given in equation (3).

(3) $6\ NO_3^- + 5\ CH_3OH \longrightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^-$

Biological denitrification was shown in the past to be an effective method for reducing nitrate concentrations in drinking water treatment facilities (Gregory and Sheiham, 1981; Hollo and Czako, 1987) as well as in sewage treatment plants (Hofmann and Hammer, 1999). In this study, we analyze denitrification in the aquarium industry and model denitrification systems in two large seawater aquaria: the Living Seas in Orlando (Florida) and Ocean Tank at the New Jersey State Aquarium in Camden (New Jersey). The two facilities have denitrification systems operating in different ways, and we use engineering parameters, empirical data and process information from both facilities to quantify their operation.

2. DENITRIFICATION AT THE LIVING SEAS

System Description

The Living Seas at EPCOT Center in Florida is the largest artificial seawater aquarium in the world, with a total volume of 23.4 million L. Most of this volume, 21.8 million L, is in the Main Tank, which contains the aquarium exhibition. At the Living Seas, reverse flow circulation is used to continually filter and disinfect the aquarium seawater. The entire volume is recirculated in 180 min at a flow rate of 129,000 L/min.

Denitrification at the Living Seas is performed on a batch basis, in a separate system. The system consists of a holding basin with a volume of 1.1 million L, and a series of biologically active denitrifying filters. The entire batch volume is taken out of the aquarium, placed into the holding basin and then recirculated through the denitrifying filters. Methanol is injected into nitrate-rich seawater as it leaves the holding basin. This water enters a 45,000 L biofilter filled with high surface area plastic rings, where the dissolved oxygen is removed during a 60 min retention time. The anoxic water is then pumped through upflow fluidized bed biofilters where bacteria reduce nitrate on the surface of carefully sized sand particles. The fluidized bed biofilters have a diameter of 20 cm and a flow rate of 0.20 L/cm^2/min. Ten fluidized bed biofilters are configured in parallel to eliminate down time during maintenance. Batch run times are a function of nitrate concentration and ambient temperature and can vary from 5 to 18 days.

Following denitrification, the batch of water is transferred to another basin where it is ozonated for disinfection and redox potential adjustment. The redox potential of denitrified seawater is typically around 200 mV, while the Main Tank values are in the range from 450 mV to 550 mV. The denitrified seawater is also treated with hydrochloric acid to decrease alkalinity, which can be greater than 10 meq/L, or more than three times higher than the average Main Tank value. Finally, after adjusting the pH to 8.1, the seawater is reintroduced to the Main Tank.

Modeling Denitrification at the Living Seas

Inorganic nitrogen speciation during a denitrification run at the Living Seas is shown in Figure 1. Nitrate concentration in both influent and effluent becomes undetectable after 6 days. The presence of nitrite as an intermediary is shown by the shape of its profile, which peaks at the same time (6 days after the start). Comparing the influent and effluent nitrite concentrations, it can be seen that nitrite production exceeds consumption for the first 5 days; afterwards, there is a net reduction of nitrite during recirculation.

Data such as those shown in Figure 1 can be analyzed to determine an empirical denitrification rate for the system. The time it takes to completely denitrify a batch of seawater in this system is given in equation (4).

$$(4) \quad t_{Denit.} = \frac{[NO_3^-]_{Init.}}{R_{Denit.}}$$

The total length of time any given batch of seawater spends out of the Main Tank is the sum of denitrification time plus the post-denitrification water treatment/transfer time. The latter quantity is defined as "operational turnover time" and is included in equation (5).

$$(5) \quad t_{Total} = t_{Denit.} + t_{Turnover}$$

The effect that a denitrified batch of seawater has on the Main Tank nitrate concentration can be determined from the ratio of their respective volumes (equation 6).

$$(6) \quad [NO_3^-]_{Decrease} = [NO_3^-]_{Init.} \frac{V_{Batch\ Denit.}}{V_{Main\ Tank}}$$

Nitrate increase in the Main Tank while a batch is being denitrified is given in equation (7). The increase is a function of the daily nitrate increase rate and the total time a batch of seawater spends out of the Main Tank.

$$(7) \quad [NO_3^-]_{Increase} = R_{Increase} * t_{Total}$$

The daily nitrate increase rate for the aquarium (in equation 7) is proportional to the feeding rate, which is in turn a function of the fish stock density.

The empirical information and the relationships defined above can be used to

develop a predictive nitrate model for the Living Seas. The model is recursive in nature: nitrate concentration at some future time is defined in terms of nitrate concentration at the preceding time interval. The time increment in the model is variable, and depends on the denitrification time of a given batch. A series of intervals is programmed to calculate the future nitrate concentrations.

The most obvious value of the modeling approach is its usefulness in answering "what-if" scenarios. Figure 2 shows predicted nitrate concentrations over a period of one year, using the original Living Seas denitrification parameters as well as two modifications. The modifications include doubling the denitrification rate (dashed line) and doubling the denitrification batch volume (center-dot line). While both modifications cause a greater nitrate decrease in the aquarium, neither one lowers the nitrate concentration in half, as might be expected. The doubled rate model lowers the concentration by less than one half throughout the time period shown in Figure 2. The rate of nitrate decrease in the doubled rate model becomes slower than that in the original model and by the end of the period, the two curves converge.

The doubled volume model lowers the nitrate concentration by less than one half for the first 9 months, but more than one half afterward. Comparison of the two modifications shows that the doubled rate model is more effective in reducing nitrate concentrations for the first 5.5 months, while the doubled volume model is more effective in the remaining time period.

Another parameter that has an effect on nitrate concentrations in the aquarium is the operational turnover time. Turnover time at the Living Seas is normally 2 days, and is thus a relatively small fraction of the denitrification time. Figure 3 shows how changes in turnover time affect nitrate concentrations after 6 months, 1 year and 2 years. All three data sets follow a linear pattern, with correlation coefficients varying from 0.968 (for the 6 month data) to 0.991 (for the 2 year data). The trends observed in Figure 3 show the large effect that changes in turnover time can have on aquarium nitrate concentrations. This effect is especially pronounced after long time intervals.

The Living Seas denitrification model can be used to develop and program a function-type expression for future nitrate concentrations (as opposed to a recursive expression developed from equations 4-7). The result shows that nitrate concentration is an exponential function of the time elapsed (Grguric and Coston, 1998), and this function can be used to determine the theoretical minimum nitrate concentration in the aquarium (equation 8). Under the Living Seas conditions discussed above, the minimum (steady state) nitrate concentration in the Main Tank is calculated as 220 μM. Equation (8) shows that, keeping all other parameters equal, the minimum nitrate concentration is directly proportional to the operational turnover time. This explains in an analytical fashion the observed relationships in Figure 3, which become progressively more linear with increasing time frame.

$$(8)\quad \lim_{t\to\infty} (NO_3^- \text{ function}) = R_{\text{Increase}} * \frac{V_{\textit{Main Tank}}}{V_{\text{Batch Denit.}}} * t_{\text{Turnover}}$$

3. DENITRIFICATION IN OCEAN TANK AT THE NEW JERSEY STATE AQUARIUM

System Description

Ocean Tank is the largest aquarium display at the New Jersey State Aquarium, with a volume of 2.9 million L. The environment on display mimics the continental shelf adjacent to the New Jersey coast, including the Hudson River Canyon. The tank contains artificial seawater of salinity 28-30 g/kg and temperature of 20°C. Flow dynamics through Ocean Tank involve surface skimming to produce a total flow rate of 16,000 L/min that is delivered to twelve parallel sand filters and treated afterward in a biofilter. Close to 10% of the total flow is disinfected by ozone in a separate line. As in the Living Seas, the volume of the entire system recirculates in 180 min.

Denitrification of Ocean Tank seawater is performed on-line, in a flow-through system. Seawater is pumped from Ocean Tank into a 2700 L deaeration tank, where methanol is continuously injected. Anoxic seawater flows from the deaeration tank into a 1500 L denitrification reactor. Large colonies of *Pseudomonas* living on a porous medium within the reactor enable denitrification to take place. Methanol is continuously injected into this environment as well. The reactor has a closed loop whose pumping rate can be used to adjust the residence time of seawater, so that denitrification proceeds to a desired extent. Seawater leaving the reactor is pumped through a foam fractionator and a sand filter. Their purpose is: (1) to aerate the seawater, (2) to remove organic compounds, and (3) to remove any particulate matter. The treated seawater is collected in an 800 L overflow tank. The flow from this tank can be directed either back into the deaeration tank (the recycle fraction) or into the aquarium, through the main water treatment system (the flow-through fraction). The relative size of these two fractions is controlled through several pumps and valves, and the system typically operates in at least 75% flow-through mode.

Modeling Denitrification in Ocean Tank

In contrast to the Living Seas denitrification system, limited water residence time in the Ocean Tank system (under 3 h) results in incomplete denitrification. The extent of denitrification can be determined by comparing influent nitrate concentrations with the sum of effluent nitrate plus nitrite concentrations (equation 9).

$$(9) \quad [NO_3^-]_{Reduced} = [NO_3^-]_{Influent} - ([NO_3^-]_{Effluent} + [NO_2^-]_{Effluent})$$

Of the two individual reduction steps, nitrite reduction to nitrogen gas (equation 2) is slower kinetically and is the overall rate-limiting step (Glass and Silverstein, 1998). Nitrite concentration in the effluent can be significant, accounting for up to 25% of effluent nitrate concentration under typical operating conditions. Release of the effluent to the main water treatment loop enables ozone and nitrifying bacteria in the biofilter to oxidize this nitrite to nitrate before the water is returned to the aquarium.

The main interest and need for modeling the Ocean Tank denitrification system is to determine the daily amounts of methanol required. Methanol in the system is used for

deaeration (deoxygenation), denitrification and bacterial growth. The amount of methanol required for deoxygenation is given in equation (10).

$$(10) \quad CH_3OH_{Deoxy.} = \frac{2}{3} * V_{Denit.} * \text{Sat. D.O.}$$

The stoichiometric coefficient 2/3 in equation (10) is based on oxidation of methanol by oxygen. $V_{Denit.}$ is the daily volume of seawater processed, calculated from the flow rate through the system. Dissolved oxygen concentration in both deaeration tank influents is close to saturation, and is given as Sat. D.O. in equation (10).

The amount of methanol needed for denitrification can be computed from the reduced nitrate concentration and the daily volume of the flow-through fraction (equation 11). Coefficient 5/6 in equation (11) is based on the stoichiometry in equation (3).

$$(11) \quad CH_3OH_{Denit.} = \frac{5}{6} * [NO_3^-]_{Reduced} * (V_{Denit.} * F)$$

The total daily amount of methanol required is given in equation (12). Factor 1.3 in equation (12) takes into account the growth requirements of Pseudomonas. These have been reported as 30% excess methanol over the stoichiometrically required amount for deoxygenation and denitrification (St. Amant and McCarty, 1969).

$$(12) \quad CH_3OH_{Total} = (CH_3OH_{Deoxy.} + CH_3OH_{Denit.}) * 1.3$$

Figure 4 shows daily methanol requirements computed using three different versions of the Ocean Tank denitrification model. The first version (represented by squares) assumes complete denitrification of all influent nitrate, with the system operating in 100% flow-through mode. This set of data provides the maximum limit on the amounts of methanol required by the system. Data represented by circles in Figure 4 are computed assuming complete denitrification, but taking into account the actual flow-through fraction during the period in question. This fraction was changed several times and the changes are reflected in the shape of the curve. The third set of data (triangles in Figure 4) are methanol requirements based on the actual amounts of nitrate reduced. Calculation of this data set includes effluent nitrate and nitrite concentrations, and thus provides the most realistic version of the model. Daily methanol requirements computed from this version are substantially lower than the maximum amounts, resulting in significant cost savings when the model is used to predict and optimize the operation of the system.

4. CONCLUSIONS

The two denitrification systems described in this study operate in different ways: the Living Seas uses a batch process where each batch is completely denitrified before it is returned to the Main Tank of the aquarium. Neither time nor the amount of methanol are allowed to limit the reactions, so the analysis of the system is based on the empirical denitrification rate. The flow-through denitrification system at the New Jersey State Aquarium has a relatively short water residence time, resulting in incomplete denitrification. Influent and effluent nitrate and nitrite data are used to determine the fraction of initial nitrate that is reduced to nitrogen gas. From this analysis, methanol requirements for the system are computed. Our approaches and results in this study show that modeling can be used to improve the operational efficiency of denitrification processes in large, closed seawater facilities.

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FIGURE CAPTIONS

Figure 1. Biofilter influent and sand filter effluent ion concentrations during a denitrification run at the Living Seas: (filled squares) influent nitrate; (open squares) effluent nitrate; (filled circles) influent nitrite; (open circles) effluent nitrite.

Figure 2. Modeled nitrate concentrations in the Living Seas after the start of denitrification: (solid line) original model; (dashed line) model with doubled denitrification rate; (center-dot line) model with doubled denitrification batch volume.

Figure 3. Modeled nitrate concentrations in the Living Seas as a function of operational turnover time: (squares) after 6 months; (circles) after 1 year; (triangles) after 2 years. Linear regression lines for the three sets of data are shown.

Figure 4. Modeled daily methanol requirements for the Ocean Tank denitrification system: (squares) needed to denitrify all influent nitrate at 100% flow-through rate; (circles) needed to denitrify all influent nitrate at actual flow-through rates; (triangles) needed to denitrify the observed fraction of influent nitrate.

Figure 1

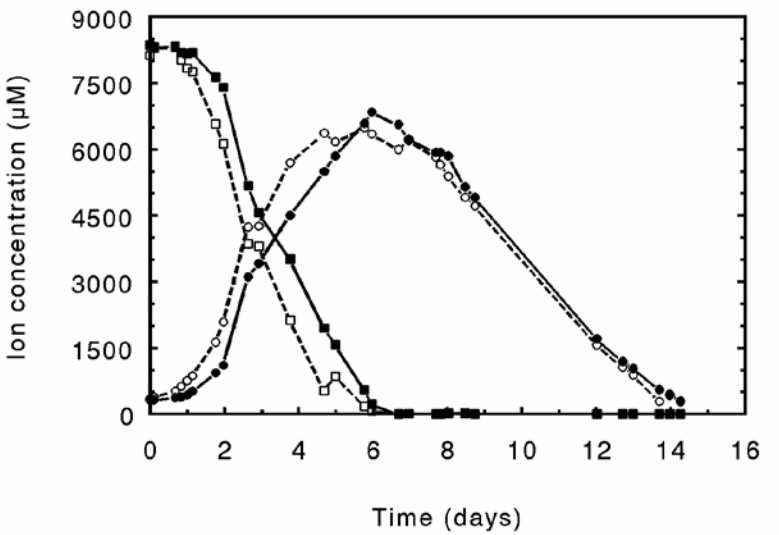


Figure 2

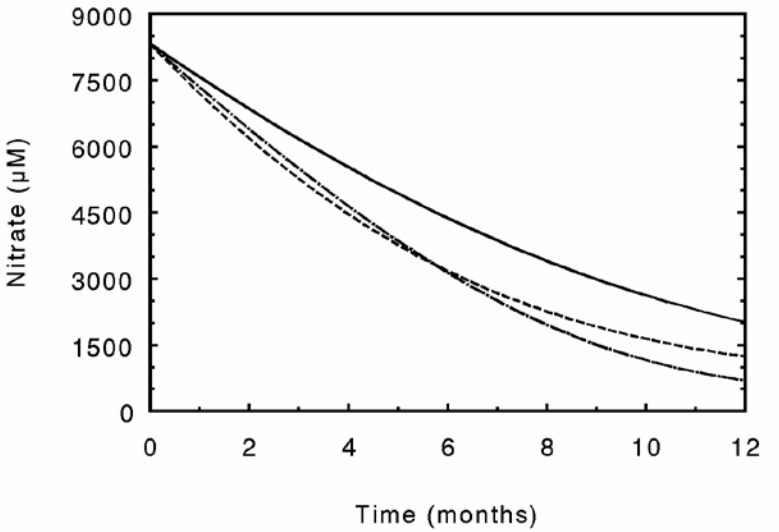


Figure 3

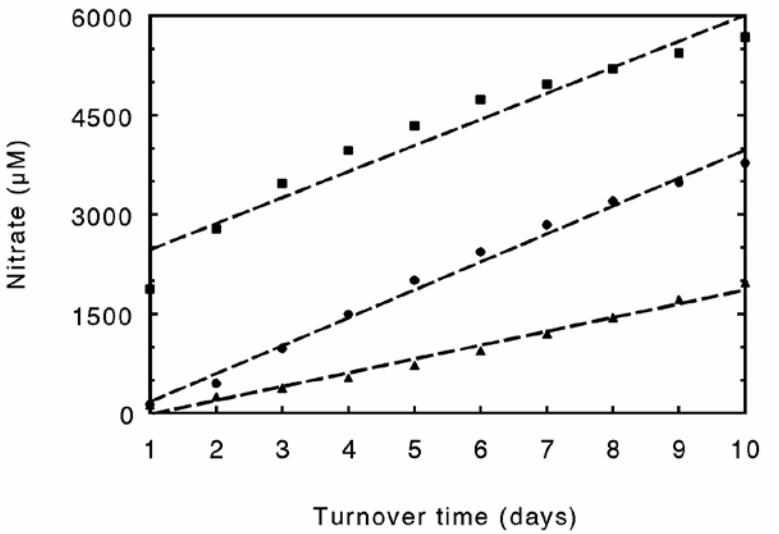
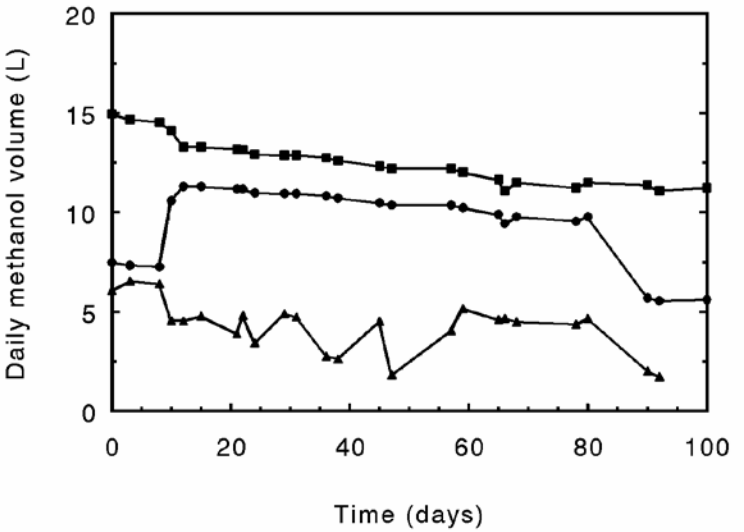


Figure 4



Sažetak

KONTROLA KONCENTRACIJE NITRATA U VELIKIM POGONIMA MORSKE VODE

Upravitelji velikih akvatorija gdje nema značajnije primarne proizvodnje i gdje su promjene vode nepraktične koriste biološku denitrifikaciju za kontrolu visokih koncentracija nitrata. Dva opisana sustava denitrifikacije u ovom radu funkcioniraju na različite načine: Sustav Živo more (Living Sea) koristi se serijskim sustavom (batch-system), dok državni akvarijum u New Jerseyu koristi protočni (flow-through) sustav. Brzina denitrifikacije kontrolira djelovanje sustava Living Sea, dok vremensko zadržavanje vode kontrolira rad sustava državnog akvarijuma New Jerseya.

Ključne riječi: nitrat, denitrifikacija, akvarij morske vode, modeliranje

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