User-Friendly Denitrification for Sustainable Life Support System Design

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Water conservation is important to most public aquariums. It is representative of the institution's conservation and sustainability initiatives, and it is also a fiscal imperative; driven by the need to minimize costs associated with seawater manufacture. Although most public aquariums embrace water conservation, "blowdown", or water replacement continues to be the most common form of nitrate reduction in exhibit life support systems. Advances in denitrification systems continue to be made, however risks associated with systems that must work within narrow tolerances, and which are susceptible to mismanagement of operational complexity, have prevented their widespread use. The National Aquarium in Baltimore employs a space-efficient sulfur-based autotrophic denitrification system that attained nitrate reduction from >300 mg/L as NO_3^- to 16 mg/L NO_3^- in an 855-m^3 mixed-species exhibit. The total footprint of the system was <8 m^2. Nitrate removal rates were high while bio-growth and bio-fouling remained low. Removal rates were in excess of 7 kg NO_3^-/m^3 S-day, which is more than three times greater than the removal rate of common autotrophic sulfur denitrification systems. Nearly 2,000 m^3 of artificial seawater has been saved in two years of operation, a value of between $43,000US and $123,000US. System cost was $0.023/Liter of exhibit volume. Operation of the system did not require elaborate control equipment such as ORP sensors or modulating valves. Operation is stable, user-friendly, and consists of only three operator functions: manual adjustment of system flow rates, filter backwashing and purging of nitrogen gas.

Introduction

There are multiple benefits to employing denitrification in aquatic life support systems: it improves water quality and the aquatic environment for animal collections by reducing nitrates; and it reduces seawater costs and supports institutional sustainability initiatives via reducing the need for employing water changes. Despite these benefits, denitrification systems are not common among aquatic life support systems: they are typically difficult or complicated to operate, are expensive, or take up a lot of space. Heterotrophic, or methanol-based, systems can be problematic due to high levels of bio-growth and bio-fouling, as well as erratic nitrate removal rates resulting in production of hydrogen sulfide. Autotrophic, or sulfur-based, systems can be oversized due to inefficient removal rates and therefore use excessive and valuable space. The National Aquarium in Baltimore has developed a denitrification system that is inexpensive, easy to operate and adds only 5% to the LSS footprint that it was retrofitted onto. The system reduced nitrate from >300mg/L to 16 mg/L in an 855 m^3 multi-taxa exhibit, and has paid for itself twice in saved seawater costs in the two years it has been running.

Nitrate - health impacts

Nitrates are an end-product of processing animal wastes that contain nitrogen. “Common” life support components such as sand filters, ozone disinfection and biofilters cannot remove nitrates. Drum filters and foam fractionators are able to slow the accumulation of nitrate in an exhibit by removing some nitrogen-bearing wastes before they are oxidized to nitrate, however nitrate accumulation will still occur even when these components are used.

In a controlled study, Morris, et. al. showed that concentrations of nitrate in excess of 308 mg/L inhibits iodine uptake and leads to goiter in bamboo sharks. In a second controlled study, Hrubec, et. al. showed that nitrate in concentrations greater than 200 mg/L lead to depressed antibody response and increased reticulocyte counts in striped bass. While elevated levels of nitrate may not be as acutely toxic as ammonia or nitrite, the referenced studies show that long-term exposure to elevated levels of nitrate cause chronic health problems for aquatic animals.

Wings in the Water Exhibit

Looking for a way to easily manage low nitrates without employing water changes, the National Aquarium developed a denitrification system for its 855 cubic meter multi-taxa exhibit called “Wings in the Water”, which was home to multiple species of elasmobranchs, teleosts and a 200 kg green sea turtle. 21 kg of food was added to the exhibit daily and the nitrate increase prior to the addition of denitrification averaged 1.6 mg/L per day.

All the water quality parameters in the exhibit were stable and within institute goals except for nitrate. Nitrate was normally managed by performing a 25% exhibit volume water change every three months resulting in one full exhibit water volume (855 m^3) exchanged each year (figure 1). Artificial seawater costs at the National Aquarium are \$22.5/m^3, therefore annual seawater costs to manage nitrate in the exhibit were

$19,200. Note that the cost of seawater manufacturing ranges among institutions worldwide, and that the National Aquarium is on the low end of the scale for artificial seawater costs. See below under "Seawater Manufacturing Savings" for further detail.

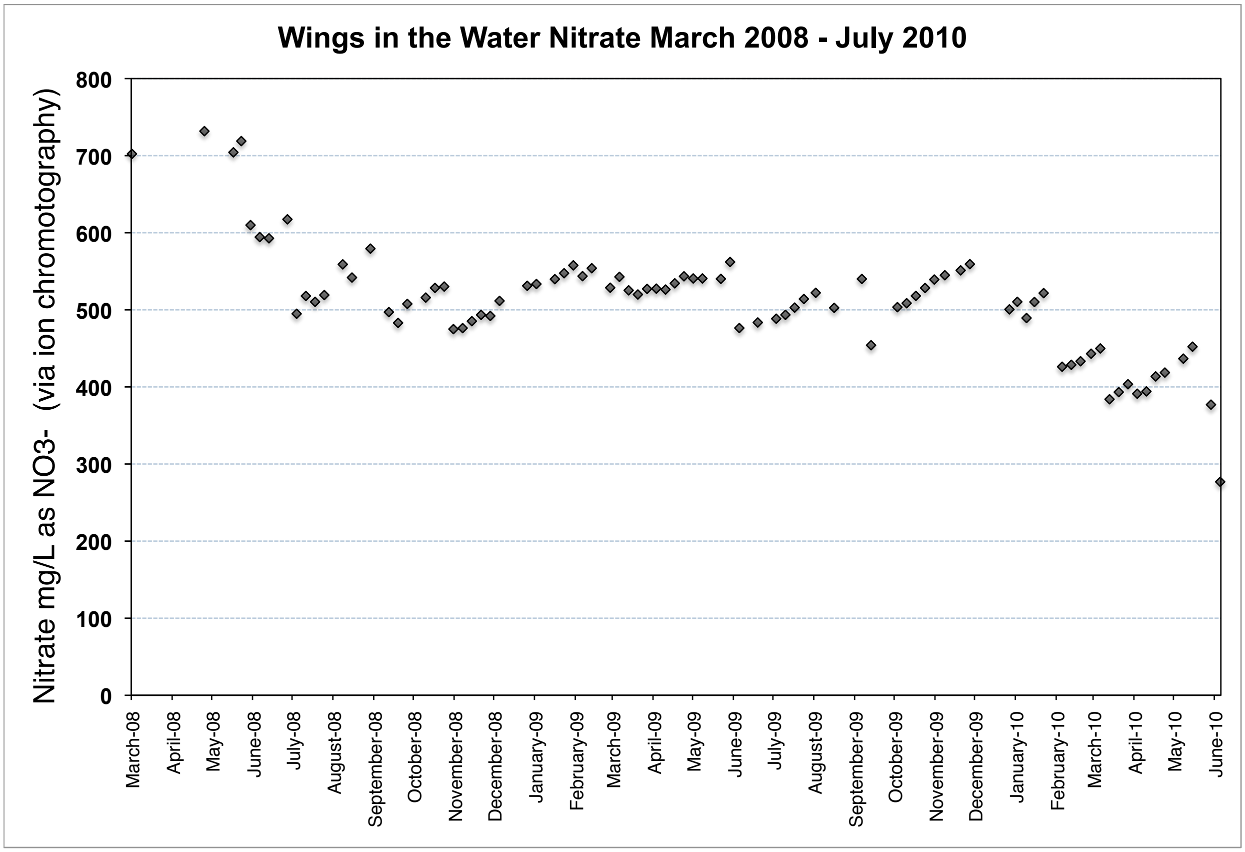

Figure 1. Nitrate in the "Wings in the Water" exhibit while managed by employing water changes. $855m^3$ of artificial seawater was used annually.

Sulfur-Limestone Autotrophic Denitrification

The system developed in Baltimore furthers the work pioneered by Michel Hignette and Sebastien Delaporte at the MAOO Aquarium in Paris in the 1990's. They applied water treatment technology that showed that in anoxic environments a strain of bacteria *thiobacillus denitrificans* thrives on elemental sulfur and reduces nitrates to nitrogen gas (figure 2). Sulfur is both the substrate that the bacteria live on and is also the electron donor or energy source for the bacteria to function. The process causes a pH drop; therefore sulfur contact is followed by contact with a buffering material such as aragonite or crushed shells, etc. (Hignette 1997).

$$11S + 10NO_3^- + 4.1HCO_3^- + 0.5CO_2 + 1.71NH_4^+ + 2.5H_2O \rightarrow$$
$$0.92C_5H_7NO_2 + 11SO_4^{-2} + 5.4N_2 + 9.62H^+$$

Figure 2. Chemical reaction describing reduction of nitrate by autotrophic bacteria with sulfur as substrate and electron donor.

The system employed at the MAOO Aquarium in Paris provided an easy to use and operate method of removing nitrates. It reduced nitrates from >300 mg/L to less than 10 mg/L in a 60 m^3 exhibit. A pump moved water upward (reverse flow) through two sulfur columns and then again through a bed of marine rubble (figure 3). Nitrate was reduced and pH was restored before water was returned to the exhibit. The removal rate attained by the system ranged from 1 – 2 kg of nitrate per day for every cubic meter of sulfur. The movement of the water through the columns was efficient because the columns were fairly narrow (40 cm diameter), so most or all of the media was utilized.

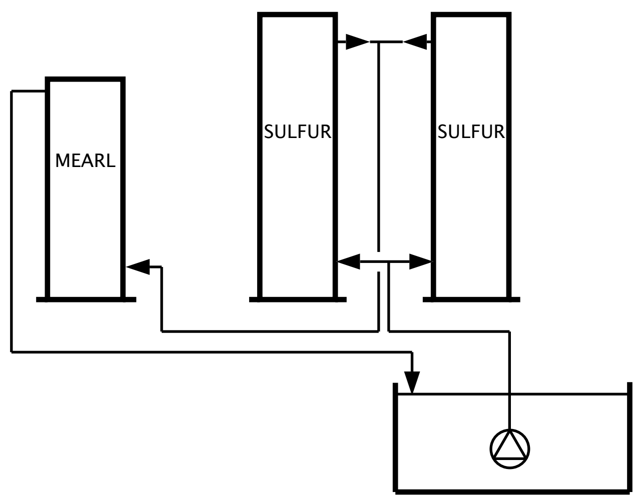

Figure 3. Schematic of sulfur-limestone autotrophic denitrification system used at the MAOO Aquarium in Paris. (Hignette, 2000).

Scaling this process up for a larger exhibit however typically requires an inordinate amount of space because of the large vessels that are required for holding sulfur and aragonite, and because the water flow through the larger vessels is typically meandering and inefficient due to larger vessel diameters, resulting in underutilization of the media.

To overcome problems of inefficiency due to scaling up, two changes were made to the system developed at the National Aquarium. First, the flow rate through the reactors is controlled independently from the flow rate from exhibit to the denitrification system. This allows the flow through the sulfur and aragonite beds to be much faster, increasing the efficiency of the process. Secondly sand filter bodies are used instead of open columnar vessels. This allows the system to be backwashed, which is necessary to maintain thin biofilms on the media. Nutrient transport to biofilms is greatest when biofilms are thin (Characklis, et. al. 1990). Thick biofilms slow nutrient transport and also clog the system. Backwashing the system three times a week maintained the highest nitrate reduction. As a result of these two changes, nitrate removal rate is in excess of 7 kg of nitrate per day for very cubic meter of sulfur. The higher removal rate allows the system footprint to occupy less space. Removal rate was calculated by adding the observed daily nitrate reduction (mg/L) to 1.6 mg/L (the historical nitrate gain seen prior to the addition of denitrification), multiplied by the system volume and divided by the total volume of sulfur.

The operation of the system is simple and involves only two steps. There is no ORP-automation which can be very unreliable, frustrating and time consuming to maintain. First, the operator opens up the gas purge valve at the top of the sulfur column. If there is a lot of gas output then he/she knows that nitrate is being reduced. Second, if the water leaving the system has an odor, it means that there is not enough nitrate present in the incoming flow. In this case, the operator turns up the incoming flow rate from the exhibit a little bit to provide more nitrate to the system. As the nitrate in the exhibit is dropping over time, the flow has to be increased to the system to provide bacteria with more nitrate. In addition to these daily operator system checks, a three times per week backwash schedule is used to maintain thin biofilms. The system uses off-the-shelf equipment and inexpensive and natural sulfur and aragonite medias. The equipment cost including media was <$20,000 US, or 2.3 cents per liter of the exhibit volume. A depiction of the system concept is shown in figure 4.

Figure 5 shows exhibit nitrate during the denitrification period. Two problems were encountered during this period; neither problem however was inherently related to sulfur-limestone denitrification. First, brass fittings were found in the pumps, resulting in copper toxicity and inhibition of the denitrifying bacteria. Once these fittings were replaced, nitrate reduction began again. Second, the building automation system that monitors and manages the overall life support system operation failed; draining 30% of the Wings in the Water exhibit, flooding the pump room and causing the denitrification system to sit idle for six days before all components of the building automation system could be replaced. The denitrification system medias were compromised and later replaced.

Note the data near the end of the denitrification period (March 2012 onward). Nitrate dropped from about 170 mg/L to 15 mg/L in seven weeks, followed by an increase to above 30 mg/L NO_3^-. The increase to 30 mg/L was the result of reducing backwash frequency from three times a week to one-and-a-half times per week. The nitrate concentration dropped again

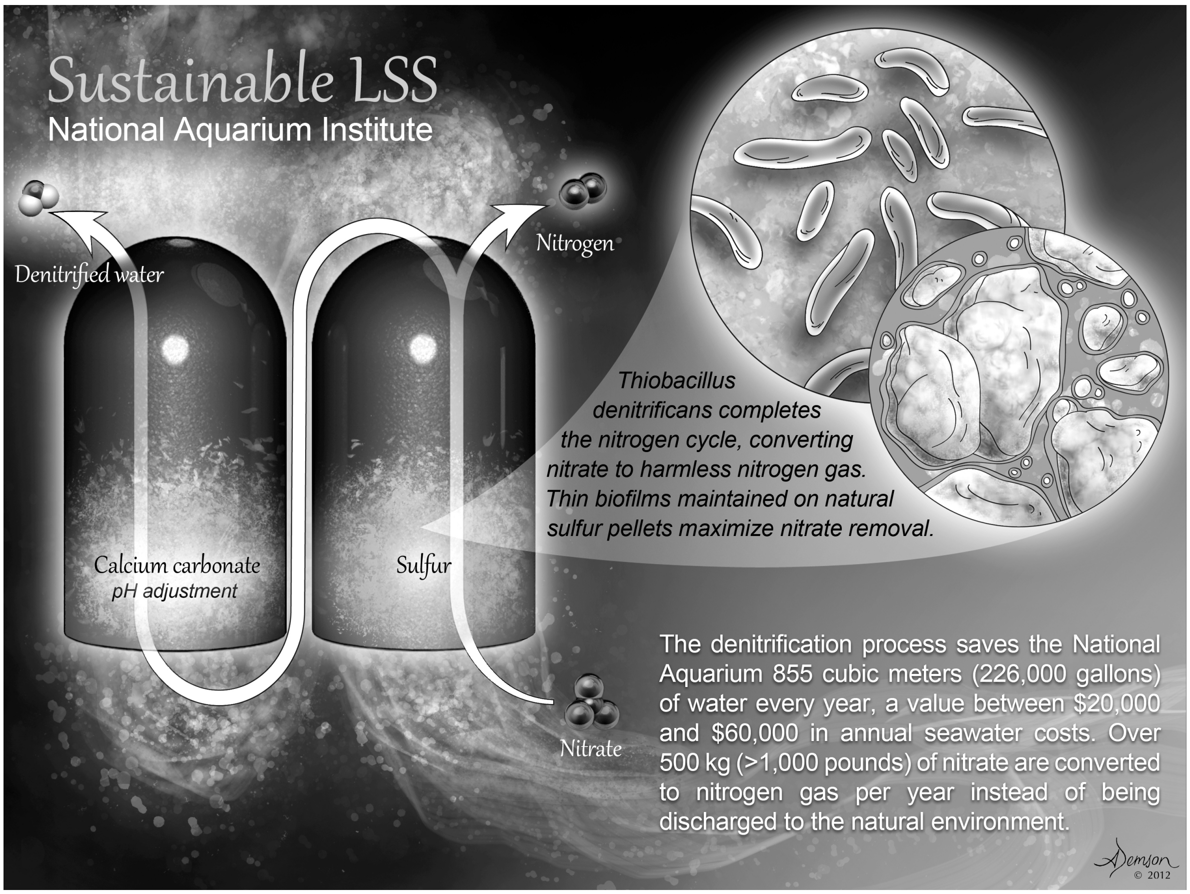

Figure 4. Depiction of the sulfur-limestone autotrophic denitrification system.

when the backwash schedule was returned to three times a week. This data emphasizes the importance of maintaining thin biofilms to maximize nutrient transport and therefore maximize nitrate reduction.

Despite the setback periods described above, five water changes were skipped while the denitrification system was operating, each batch normally costs the National Aquarium $4,800US. The Wings in the Water exhibit was shut down in early September 2012 for renovation. The low nitrate water from the exhibit was used in other exhibits and holding systems, saving an additional $19,000US in seawater manufacturing costs. Prior to exhibit shut down, the denitrification system was connected to another moderately sized exhibit, the 1,230 m^3 “Atlantic Coral Reef” which is home to a variety of elasmobranchs and teleosts, has a daily food load of 15 kg and a daily nitrate increase of 0.4mg/L (prior to denitrification). At the time of writing, the denitrification system has reduced nitrate 22% there, from 251 mg/L to 195 mg/L. Further seawater manufacturing cost savings are expected.

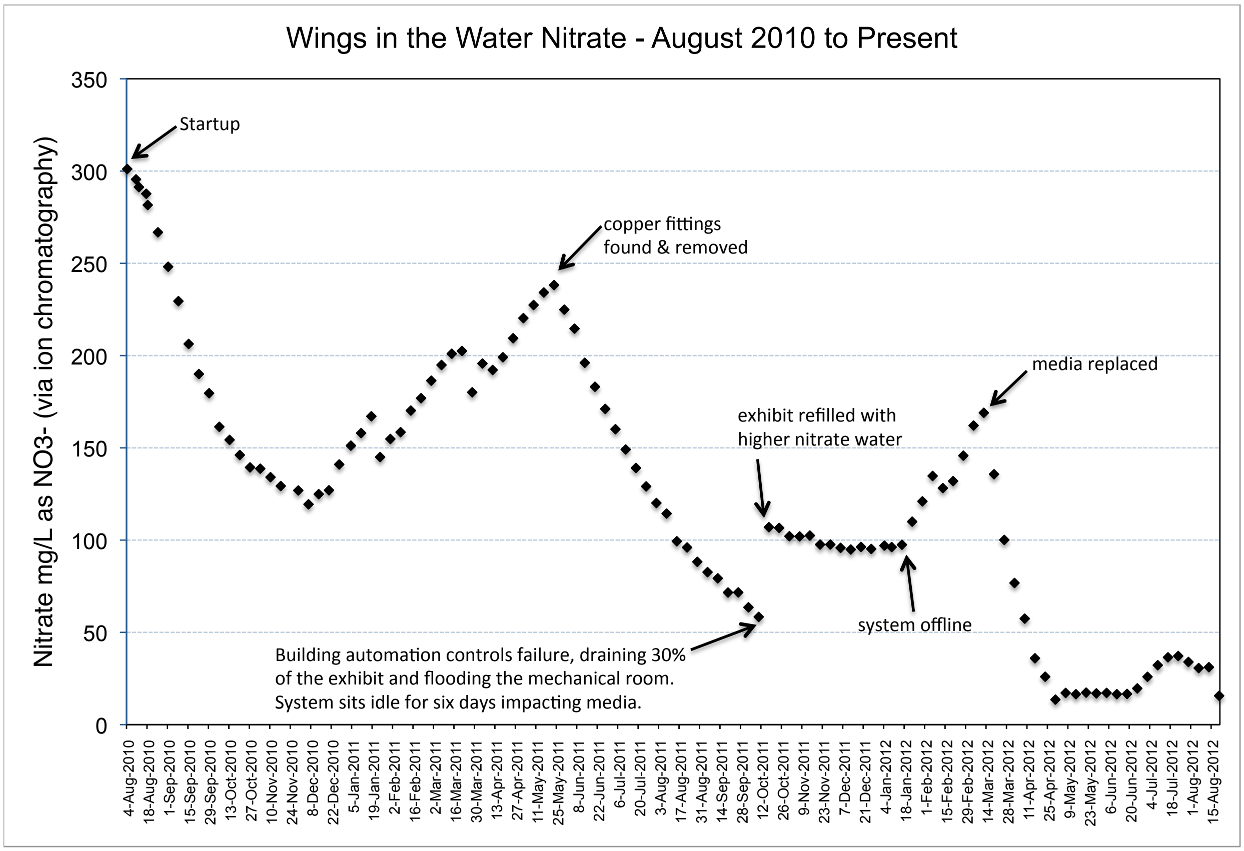

Figure 5. Nitrate reduction from >300 mg/L to 16 mg/L via autotrophic denitrification. Maximum removal rates exceeded 7 kg NO_3^-/m^3 of S-day during this period. Two events not inherently related to sulfur-limestone denitrification occurred that slowed overall nitrate reduction. Copper-bearing fittings inhibited bacterial growth from December 2010 to May 2011 before they were found and removed. And a building automation system failed, draining 30% of the exhibit and flooding the mechanical room; causing the denitrification system to sit idle for six days which compromised the bacterial populations and medias from September 2011 to January 2012.

Seawater Manufacture Savings

Seawater costs vary widely among institutions worldwide (figure 6). The savings given above for the “Wings in the Water” exhibit are derived from the low end of the range of artificial seawater costs ($22.5/m³). Savings achieved can be much greater, depending on the cost of seawater manufacture that an institution pays, as well as frequency of water changes that it practices.

	Euros	US $
Artificial SW:	€18 - € 50/m³	$22 - $63/m³
Natural SW:	€ 6 - € 60/m³	$ 7 - $76/m³

Figure 6. Seawater cost ranges. *(*McEwan, et. al.) Data adjusted12% for inflation.

Institutions are under increasing pressure to find new ways to increase income streams and also to reduce operating costs. Utilizing the technology discussed above provides practical operating cost reduction and has the added benefit of increasing sustainability of the institution's operations. Even if seawater is obtained free of charge, using denitrification allows water to be returned to the natural environment with less nutrient load.

Sustainable Life Support System Design

The purpose of a life support system is to provide a stable and healthy environment that supports longevity of aquatic animals. The success or failure of a life support system to achieve this goal is measured in water quality parameters. Many systems fail to meet this goal and when all else fails, water changes are typically employed to bring water quality parameters back to desired levels. This practice is used in order to provide a healthy environment for animals held in the system, but from the standpoint of resource requirement it means that the life support system design is not very sustainable.

Sustainability is also measured in terms of environmental impact. When water changes are employed, nitrate-laden water is commonly discharged either directly to the natural environment or to a wastewater treatment plant. Unless the given wastewater treatment plant is equipped with tertiary (denitrification) treatment, the nitrates pass through the plant and end up in the natural environment. For example, employing water changes to mange nitrate in the Wings in the Water exhibit meant that >500 kg of nitrate was being dumped to the natural environment every year. While a small amount of natural denitrification can occur in some aquifers, the overall impact of natural denitrification is minimal and cannot keep up with the constant load of nutrient pollution. Note that the amount of nutrient pollution coming from public aquaria is not a major contributor compared to other point sources such as wastewater treatment plants; however the practice is contrary to the missions of many aquarium institutions, which are increasingly in the business of being "stewards of the aquatic environment". While adding denitrification to our life support systems may not save the health of the planet, it does add sustainability to aquarium operations by reducing the need to perform water changes. One must also consider the reduced "carbon footprint" resulting from shipping fewer artificial salts to make seawater.

A sustainable life support system is one that provides a stable and healthy aquatic environment but does so at a minimum of resource requirement (water, power, labor, space, etc.) meaning that it is not only sustainable for the animals, but also for the institution's operations costs. It also means that the system minimizes negative impact the natural environment.

Conclusions

Denitrification adds sustainability to life support system design and operation: reducing nitrates to nitrogen gas via natural bacteria, sulfur and aragonite. Water quality is improved, water use is reduced, operations costs are reduced and environmental impact is minimized.

A sulfur-limestone autotrophic denitrification system developed at the National Aquarium in Baltimore furthers the work pioneered by the MAOO Aquarium in Paris in the 1990's. The system is made space-efficient by controlling flow rates to reactors independently from process flow, and by using vessels that allow frequent and aggressive backwashing. Nitrate in an 855 m^3 multi-taxa exhibit ("Wings in the Water") with a daily food load of 21 kg and daily nitrate increase of 1.6 mg/L was reduced from >300 mg/L to 16 mg/L. Maximum removal rates exceeded 7 kg NO_3^- per m^3-day. The system footprint occupies less than 8 m^2. System operation is controls-free and user-friendly, consisting of a daily manual gas purge, occasional manual flow rate increase, and a regimented backwashing schedule to maintain thin biofilms. System cost was $0.023/Liter of exhibit volume.

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