Internal Nutrient Loading in the Crystal Springs Reservoirs

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Abstract

Internal loading is a process that occurs in lakes and reservoirs when nutrients are introduced into the water from the lake sediment. Along with external loading, internal loading can lead to lake eutrophication and cause chemicals to enter the water, causing taste, odor, and color problems. Internal loading can also begin a positive feedback loop that intensifies eutrophication. These problems are especially important if the lake is used as a drinking water resource. This experiment studied the Crystal Springs reservoirs in San Francisco, a pair of reservoirs that have the potential of becoming eutrophic from proposed chloramine disinfection that would increase nitrogen loading. A chamber study was developed that determined the internal loading potential of the two reservoirs and the effectiveness of hypolimnetic aeration as a solution. Two samples of undisturbed sediment and hypolimnetic water were taken from each reservoir and stored in study chambers. The redox potential and concentrations of phosphate, ammonia, and nitrate were monitored in these chambers through oxic, anoxic, and restored oxic conditions. Redox levels dropped in the chambers during anoxia to levels as low as -430 mV in the upper reservoir and -635 mV in the lower reservoir, while phosphate and ammonia increased to peaks of 661 ug/l and 430 ug/l in the upper reservoir and 714 ug/l and 906 ug/l in the lower reservoir. The increase of phosphate and ammonia in the chambers indicated that internal loading occurred in anoxic conditions. Nutrient concentrations decreased with aeration below detectable limits of 50 ug/l, suggesting that hypolimnetic aeration could be a good technique to eliminate future internal loading that could occur with increased productivity from chloramine based nitrogen loading.

Introduction

Lake eutrophication is marked by an increase in productivity caused by an excess of nutrients. The process begins when nutrients that limit growth, most frequently phosphorous and nitrogen, enter the system through natural or human processes and stimulate algal blooms (Horne and Goldman 1994). When algae populations increase, many problems can occur. Lake water loses its natural clear blue color and becomes green, causing a loss of transparency. Intense eutrophication can produce large floating mats of algae, commonly cyanobacteria, that can produce odors and appear unpleasant to lakeside residents. The increased populations of algae lead to larger amounts of algal biomass that sink to the lake bottom and consume oxygen during decomposition. In the hypolimnion, or the lower level of the lake, oxygen levels can be depleted by decomposing biomass resulting in anoxia.

An anoxic hypolimnion can pose many problems. Fish cannot breathe without oxygen in the water, therefore anoxia can cause significant fishkills in a lake. Zooplankton populations can also decline when a hypolimnion becomes anoxic. To avoid predation by fish, zooplankton hide in lower waters during the day and come up to the surface waters to feed at night (Horne and Goldman 1994). When the hypolimnion becomes anoxic, the zooplankton lose their refuge in the hypolimnion, beginning a positive feedback loop. Anoxia caused by increased algae leads to a decrease in population of zooplankton, an algal predator. As conditions become more reduced in the hypolimnion, bacteria begin producing hydrogen sulfide, using sulfate instead of oxygen as a terminal electron acceptor (Beutel 1999, pers. comm.). Hydrogen sulfide is poisonous to fish, and can become an odor problem for people who live near a lake or use its waters as a drinking water resource. Manganese and iron are also released from the sediments in reduced conditions, and along with hydrogen sulfide can cause taste, odor, and color problems.

Two sources of nutrients can lead to eutrophication in lakes and reservoirs. External loading occurs when runoff from the watershed brings in nutrients from anthropogenic sources, such as sewage plants and agricultural runoff, and from natural sources. Frequently, external loading is the main determining factor in a lake's trophic status because of its large scale (Horne 1998). In addition, when a lake has an anoxic hypolimnion, nutrients can enter the water column from the sediment in a process known as internal loading (Bostrom *et al.*

1988). The two most important nutrients that can be introduced by internal loading are phosphorous and nitrogen.

Phosphorous loading can increase the amount of soluble reactive phosphate that is available for algal growth in a lake or reservoir. In oxic conditions, phosphate bonds with oxidized iron (Fe^{3+}), forming an insoluble precipitate in the sediment (Hupfer *et al.* 1995). Once oxygen is absent from the environment, microorganisms use oxidized iron as a terminal electron acceptor and reduce Fe^{3+} to Fe^{2+}, releasing soluble phosphate and iron into the pore water of the sediment and thus into the water column above (Mitchell and Baldwin 1998). If algal growth in a lake is phosphorous limited, this loading produces a positive feedback loop in which a lake becomes more eutrophic from increased phosphate loading. Hypolimnetic anoxia initiates internal phosphate loading, which stimulates further algal growth, leading to more intense hypolimnetic anoxia.

Hypolimnetic anoxia can also cause a shift in the nitrogen cycle, resulting in increased ammonia levels in the hypolimnion (Vincent and Downes 1981). Under normal conditions, organic nitrogen in the sediment is converted to ammonia through ammonification. If oxygen is present, ammonia is converted to nitrate through nitrification or converted to organic nitrogen in the sediment. Nitrate is then denitrified by bacteria under anoxic conditions into nitrogen gas and thus leaves the water system. However, when the system becomes anoxic, biological ammonia uptake in the sediment declines, since the process is then performed by anaerobic bacteria that grow at a slower rate than the aerobic bacteria that uptake ammonia in normal conditions. An anoxic system also stops the process of nitrification and thus prevents denitrification from occurring. These two factors lead to a buildup of ammonia in the hypolimnion in anoxic conditions.

Several techniques have been used in the past to solve productivity problems caused by the two forms of nutrient loading. Two common methods are reduction of external nutrient loading and hypolimnetic aeration, which eliminates internal loading by restoring dissolved oxygen levels in the hypolimnion (Prepas and Burke 1997). Before adopting a method to reduce eutrophication in a lake, both internal and external sources must be analyzed to determine which has the greatest influence on algal growth. However, most drinking water reservoirs have protected watersheds that greatly reduce the amount of external nutrients entering the water, thereby making external loading minimal. Therefore, internal nutrient

loading is frequently the limiting factor that determines productivity in drinking water reservoirs, since significant amounts of nutrients only enter the system from the sediment.

This experiment studied the upper and lower Crystal Springs Reservoirs (maximum depth 27m and 34m, respectively), two drinking water reservoirs south of San Francisco that have a protected watershed and therefore minimal external loading. The water comes from the Hetch Hetchy Reservoir through a 160 km aqueduct. The lower reservoir has been observed to be more eutrophic than the upper reservoir. Short term anoxia has been witnessed in the hypolimnion of the lower reservoir, which indicates that internal loading may be occurring during this period without oxygen (Beutel 1999, pers. comm.).

The incoming water is currently sanitized with chlorine gas before it enters the reservoir. Because of the dangers of working with chlorine gas, the utility is planning to switch to use of chloramines for disinfection in 2003. This is a much safer alternative that reduces the amount of potentially carcinogenic by-products that are formed (SFPUC 1999). When chloramines enter a lake system, the molecules break down into chlorine and ammonia. An addition of ammonia will cause increased nitrogen loading to the system and perhaps increase productivity, which may lead to intensified hypolimnetic anoxia.

Earlier work on the Crystal Springs reservoirs done during the summer of 1999 indicated that internal loading would occur in an artificially anoxic environment (Beutel 1999, pers. comm.). Phosphate and ammonia levels increased after oxygen was purged from the system. The study preserved sediment samples in chambers that could be turned oxic or anoxic while being monitored.

This experiment first assessed the potential for internal loading of the Crystal Springs reservoirs by creating an artificially anoxic environment. The existence of internal loading was determined by monitoring nutrient concentrations, which increased under reduced conditions, illustrating that internal loading was in progress. Secondly, once internal loading was occurring, this experiment studied the effectiveness of aeration as a means to halt the loading process. If internal loading occurred in an anoxic environment, then in theory it would be halted if oxic conditions were restored.

Methods

To assess internal nutrient loading in the reservoirs, a laboratory chamber study of sediment samples was conducted. The chambers were initially monitored under aerated conditions to determine the release of nutrients under oxic conditions. The chambers were then driven to anoxia to determine if internal loading occurred. Once the chambers reached a steady state after a month in anoxia, they were aerated to determine if nutrient loading ceased. Throughout the oxic/anoxic/oxic treatments, the redox potential along with ammonia, phosphate, and nitrate levels were measured to determine if oxygenation could be a good method to prevent internal loading in the reservoir.

The chambers were designed to study the sediment/water interface in the reservoir. Samples of the lake sediment were collected from both reservoirs at previously determined sites in the middle of the reservoir. The chambers used were identical to those used in previous studies, since they were proven to be an effective and inexpensive method for studying the sediment/water interface (Beutel 1998). Only one site was used at each reservoir since it has been shown in other lakes that sediment/water interactions are not significantly different among spatially different sites (Auer *et al.* 1993). An Eckman Dredge was used to collect the sediment from the lake bottom. The dredge was brought up to the surface from the lake bottom with about 15 cm of undisturbed sediment and some water from the hypolimnion. The chamber was then lowered into 5 cm of the sediment and cupped by hand to prevent sediment disturbance as the chamber was lifted from the dredge and the bottom of the chamber was tightened into position.

The chamber was then carefully filled with water from the hypolimnion that was collected with a Van Dorn sampler. The Van Dorn is a cylindrical container that holds about a liter of water, which can be snapped shut with the use of a messenger to sample water from a desired depth (in this case directly above the lake bottom).

The storage chambers used were clear plastic cylinders measuring 30 cm tall and 10 cm in diameter. The sediment occupied the lower 5 cm of the chamber beneath a liter of water. The chamber was sealed at the top, but contained a tube that could be used to either gently bubble air into the water or withdraw a water sample with a syringe. There were also upper and lower probes in the container that were used to measure the redox potential of the water

in the chamber as a means of measuring the severity of reduced conditions in the water column.

Four chambers were set up, using duplicate samples taken from the Upper and Lower reservoirs. The chambers were preserved by incubation at 14^{o}C (the temperature of the hypolimnion) and aeration, which simulated oxic conditions. The chambers remained aerated for two weeks to serve as a comparison against the next anoxic step. Water samples of 50-100 ml were taken twice a week from the chambers. Sample water was replaced with an equal volume of distilled water in order to maintain the same volume without adding to the nutrient concentration. While this process did cause a slight dilution of the chamber water, previous studies have determined that the nutrient concentration is not significantly altered by the process (Beutel 1999, pers. comm.).

After the chambers had been aerated for two weeks and it was determined by the stability of readings of the redox potential meters that the chambers were in a steady state, the chambers were turned anoxic. Nitrogen gas was bubbled into the chambers instead of air, purging the oxygen in the chambers through a one way exit valve that prevented outside air from entering the chambers. Water samples were still taken twice a week and replaced with distilled water that was bubbled with nitrogen to purge any oxygen that might have been present.

The collected water samples were filtered through 45 um Whatman filter paper and stored frozen. Samples were later defrosted and tested for presence of phosphate, nitrate, and ammonia using relatively simple and reliable colorimetric methods. The detection limits of the phosphate and ammonia tests were 50 ug/l.

Once the chambers became anoxic, additional samples were taken whenever the water smelled of rotten eggs, the telltale sign of hydrogen sulfide. These samples were preserved with zinc acetate and sodium hydroxide, driving available hydrogen sulfide to S^{2-}. The sulfide concentrations were later quantified by a colorimetric method with a detections limit of 0.1 mg/L.

Once the chambers reached an anoxic steady state after a month, they were re-aerated in order to restore oxic conditions. As with the earlier oxic and anoxic phases, samples from the re-aerated chambers were taken and preserved for later analysis. The chambers continued to be aerated until equilibrium was reached after an increase in redox potential.

Results

The results for redox potential readings along with phosphate, ammonia, and nitrate concentrations from the four chambers are presented in Figures 1 through 4. Note that the dotted lines through days 15 and 58 indicate the beginning and end of the anoxic period. As indicated in the legend of each figure, the data points from each reservoir share a common shape, but differ in shading. All four of the graphs share a common time scale as well.

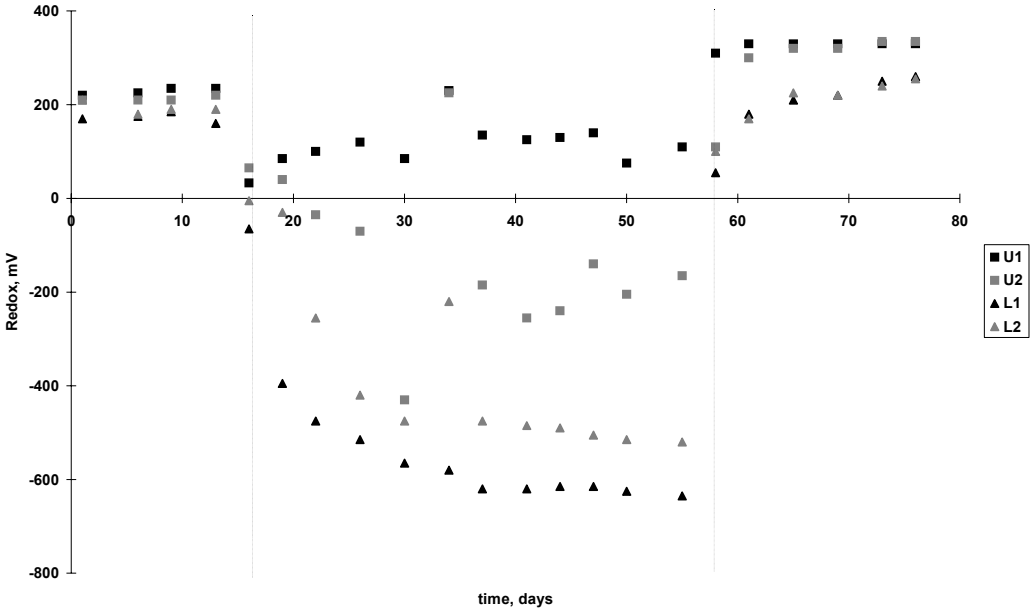

Figure 1. Redox potential in the Crystal Springs chambers. Dotted vertical lines indicate the beginning and end of the anoxic period. U1 and U2 are the chambers sampled from the Upper Reservior, and L1 and L2 are the chambers sampled from the Lower Reservior.

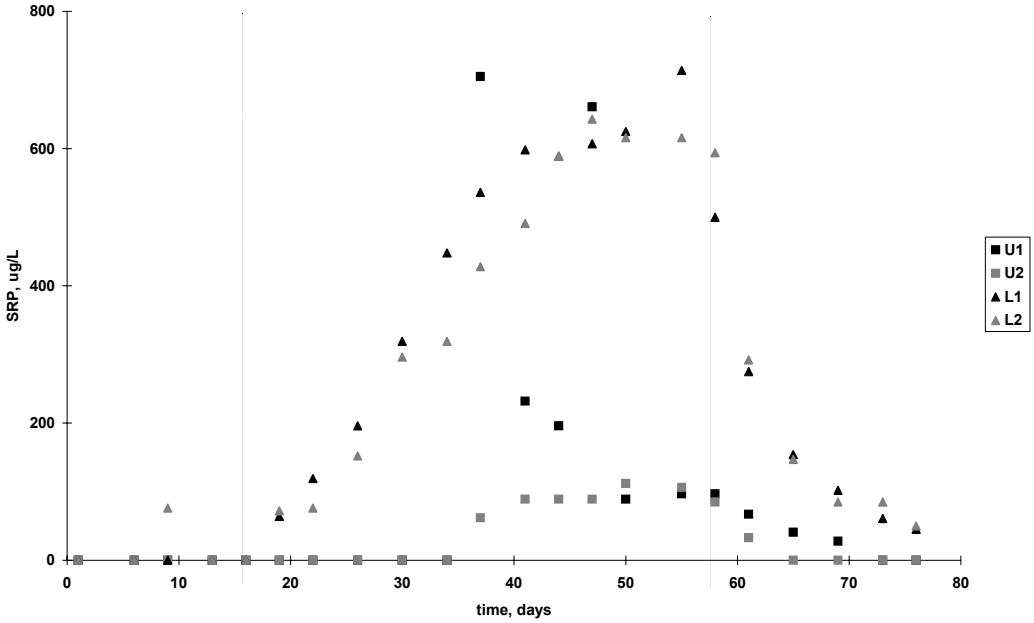

Figure 2. Phosphate concentrations in the Crystal Springs chambers. Dotted vertical lines indicate the beginning and end of the anoxic period. U1 and U2 are the chambers sampled from the Upper Reservior, and L1 and L2 are the chambers sampled from the Lower Reservior.

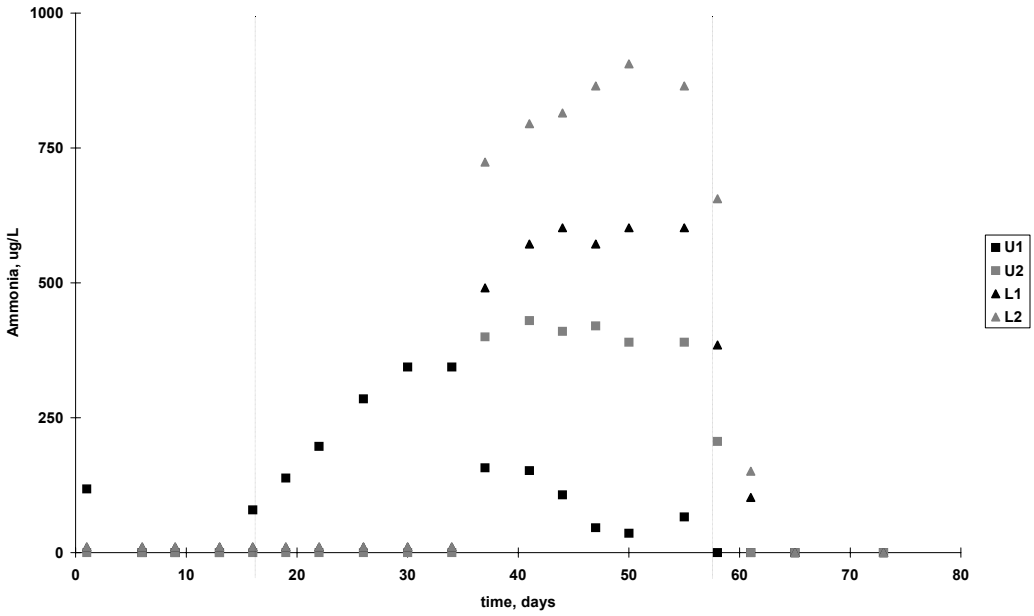

Figure 3. Ammonia concentrations in the Crystal Springs chambers. Dotted vertical lines indicate the beginning and end of the anoxic period. U1 and U2 are the chambers sampled from the Upper Reservior, and L1 and L2 are the chambers sampled from the Lower Reservior.

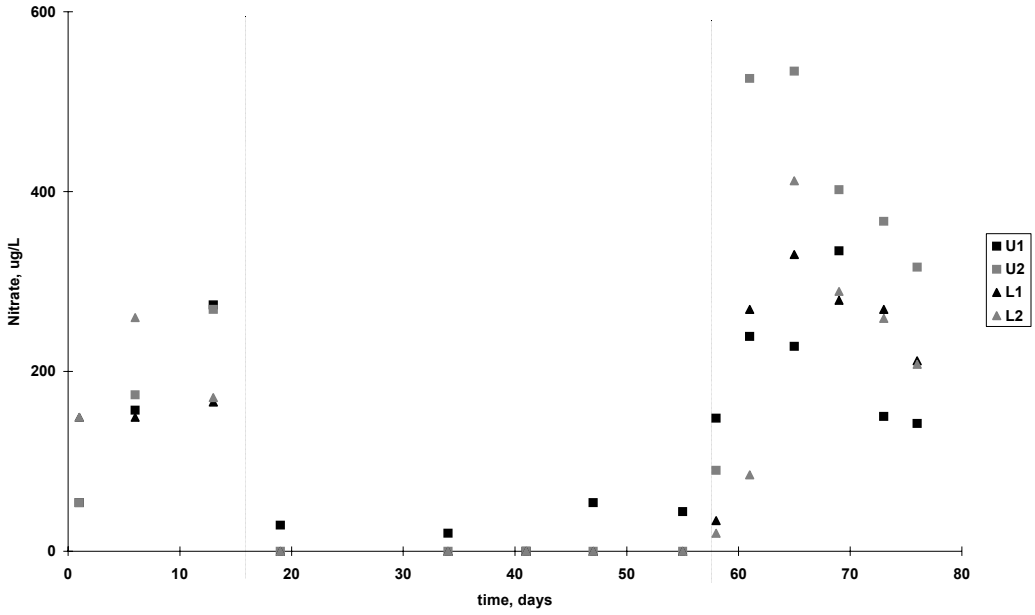

Figure 4. Nitrate concentrations in the Crystal Springs chambers. Dotted vertical lines indicate the beginning and end of the anoxic period. U1 and U2 are the chambers sampled from the Upper Reservior, and L1 and L2 are the chambers sampled from the Lower Reservior.

During the oxic stage of the first two weeks, redox potential was measured to be 220 mV and 230 mV for the two chambers from the upper reservoir (U1 and U2, respectively) and 190 mV and 200 mV for the two chambers from the lower reservoir (L1 and L2, respectively). Phosphate and ammonia levels remained below detectable limits. Nitrate levels rose from 66 ug/l and 65 ug/l for U1 and U2 to 275 ug/l and 280 ug/l at the end of the period, while L1 and L2 remained relatively stable, with final concentrations of 166 ug/l and 171 ug/l.

Once the chambers were turned anoxic on day 15, redox levels began declining. U1 and U2 dropped somewhat erratically, reaching minimums of 75 mV and -430 mV. Redox potential in L1 and L2 dropped more smoothly, reaching minimums of -635 mV and -520 mV.

Nutrient levels of the chambers became detectable during this period. Phosphate analysis showed levels in U1 increasing smoothly to 230 ug/l, with the exception of two peaks of 705 ug/l and 660 ug/l, while U2 steadily increased to a peak of 112 ug/l. L1 and L2 both exhibited the same trend of phosphate increase, leading to peaks of 714 ug/l and 642 ug/l,

respectively. Nitrate levels were below detectable limits in all of the chambers during this stage except U1, which had a concentration of 54 ug/l on day 47. Ammonia levels reached peaks of 344 ug/l and 430 ug/l in U1 and U2, while levels in L1 and L2 began increasing on day 36 to peaks of 602 ug/l and 905 ug/l.

After the chambers were re-aerated on day 58, redox levels began increasing in the chambers. U1 stabilized at 330 mV, compared to U2 at 335 mV, L1 at 260 mV and L2 at 255 mV. By the end of this third period, phosphate levels dropped below detectable limits in the chambers from the upper reservoir, while the chambers from the lower reservoir both dropped to a level of 42 ug/l. Ammonia levels also dropped below detectable limits in all of the chambers during this time. Nitrate levels increased to 40 ug/l and 69 ug/l in U1 and U2 and 68 ug/l and 49 ug/l in L1 and L2.

During the anoxic period, six hydrogen sulfide samples were taken from the lower reservoir chambers. While sulfide should have been detected in periods when redox levels dropped below a value of -400 mV and the samples gave off the odor of rotten eggs. However, no hydrogen sulfide was detected in any of the samples collected, despite a detection limit of 0.1 mg/l.

Discussion

During the three stages of the experiment, the redox levels followed the predicted pattern of decrease in anoxic conditions. In three of the four chambers, the readings dropped below 0 mV. The lower reservoir chambers had lower redox levels than the chambers from the upper reservoir, likely due to the fact that the lower reservoir is more eutrophic. These results indicate the severity of reduced conditions in the chambers during anoxia and were used to determine when to end the re-aeration phase after the chamber had reached equilibrium.

The large differences between U1 and U2 redox potential levels cannot be entirely explained. While the trend of redox reduction in U1 was visible, the magnitude of measured levels differed significantly from U2. The reasons for this difference are uncertain, and perhaps further replication is needed in order to explain the results of the two chambers. More differences in the results of the nutrient concentrations in U1 will be discussed later. The outlying spike seen on the redox graphs on day 34 occurred when the nitrogen cylinder

used to purge out the oxygen in the sealed chambers went empty. The cylinder was replaced within two days, but the redox levels rose temporarily.

Trends in the concentrations of soluble reactive phosphate in the chambers matched the predicted response. Under aerated conditions in the beginning of the study, phosphate levels in the chambers were below detectable limits; any phosphate in the system was bonded to iron as an insoluble precipitate in the sediment. The spike seen in the L2 chamber on day 9 is most likely anomalous or caused by an error in the testing method.

When the chambers were turned anoxic, bacteria began reducing Fe^{3+} to Fe^{2+}, which broke the bond between iron and phosphate, releasing soluble reactive phosphate into the water, leading to the increases seen in the figures. U1 had an unusual pattern of increase with two large spikes at days 37 and 47, which again might have been caused by testing error. L1 and L2 demonstrated larger scale release, reaching peaks of 715 ug/l and 642 ug/l, versus peaks of 230 ug/l and 106 ug/l in U1 and U2 (ignoring the anomalous spikes in U1). These results were predicted since the lower reservoir is more eutrophic and therefore has a larger amount of phosphate in the sediment.

Once the chambers were re-aerated, oxic conditions were restored and the available phosphate returned to an insoluble precipitate in the sediment, causing measured levels of soluble reactive phosphate to decline. In all of the chambers the levels of phosphate declined significantly by day 73.

Unlike the other monitored nutrients, nitrate was present in the water column during aeration. Nitrate in Upper Crystal Springs (UCS) increased during initial aeration while concentrations in Lower Crystal Springs (LCS) remained stable. While the reasons for the presence of nitrate at this stage is uncertain, the decline during anoxia was predicted by the shift in the nitrogen cycle. In anoxic conditions, the process of nitrification is halted and therefore nitrate production ceases. All available nitrate is denitrified into nitrogen gas, which then exits the system. All of the chambers measured minimal nitrate during this time with the exception of U1, which had low levels compared to oxic conditions. The increase in nitrate after aeration was most likely a result of nitrification beginning again under aerated conditions, converting the high levels of ammonia to nitrate.

Levels of ammonia were undetectable in the initial aerated phase of the experiment in all of the chambers, with the exception of a spike in U1 on day 1. This is because any ammonia

in the system was locked up in the sediment or converted to nitrate. The spike in U1 is most likely a result of a testing error during ammonia detection. If the spike were accurate, it might explain the increase in nitrate levels in UCS during the initial oxic stage as initial ammonia was converted to nitrate. However, since nitrate concentrations in both UCS chambers rose during this stage, the spike is likely a testing error.

During anoxia the process of nitrification stopped, leading to the accumulation of ammonia in the water column. Biological ammonia uptake was also reduced because of slow-growing anaerobic bacteria in the sediment. These two factors led to an increase in concentrations of ammonia in the chambers.

An apparent oddity seen from the figures is the fact that ammonia levels weren't detected for the U2, L1, or L2 chambers until day 37. This unpredicted trend may be explained by the fact that the samples from day 37 and beyond were tested separately from the first half of samples. Perhaps the two different applications of the previously erratic colorimetric method caused the inconsistences in the results. However, the U1 data follows a different pattern, increasing to a peak at day 37, then gradually decreasing. While the UCS displays an expected mean pattern, the variances between the two chambers cannot be explained.

Despite the trend of increase of ammonia levels in the chambers, the scale of increase was noticeably higher in the lower reservoir. This is consistent with the predicted results, because the lower reservoir is a more eutrophic system.

Once oxic conditions were restored on day 58, nitrification resumed and the rate of biological ammonia uptake increased, leading to a decrease in ammonia concentrations. This decrease occurred more rapidly than the phosphate levels, and was undetectable in all of the chambers by day 65.

Contrary to predicted results, hydrogen sulfide was not detected at any point in any of the chambers. This was despite the fact that the rotten egg smell was detected in the lower reservoir during the latter days of the anoxic period. This may be explained by faults in the testing method or a poor nose on the part of the sampler. The odor threshold of hydrogen sulfide might also be below the minimum detection limits (0.1 mg/L) used in the colorimetric test, in which case hydrogen sulfide could have been present at a concentration that was undetectable by the testing method.

The trends illustrated in the results of this study indicate that both reservoirs have the potential for internal loading. In current conditions, the chlorinated waters are productive enough to have nutrient-rich sediment that can release phosphate and ammonia into the water column under anoxic conditions. Therefore, it is very likely that internal loading could occur if the system were more productive as a result of increased ammonia loading from chloramine sanitation. This would especially be true if the reservoir were nitrogen-limited, or where ammonia and nitrate levels were the determining factor in limiting algal growth. The actual limiting nutrient of the reservoirs is currently under debate. Arguments exist for both phosphorous and nitrogen limitation as well as the possibility of co-limitation of both nutrients.

The chamber study did suggest that the upper reservoir had less intense loading than the lower reservoir. This may indicate that the upper reservoir is less at risk of internal loading, especially considering that anoxia has never developed in its hypolimnion. However, the data did show a release of both phosphate and ammonia in anoxic conditions. Despite the fact that this release would not occur under current conditions that never reach anoxia, the potential for release exists and could pose a problem when stimulated by increased productivity from chloramine-based nitrogen loading.

The presence of internal loading in the lower reservoir is more evident. Since periods of anoxia have been witnessed, it is likely that internal loading occurs when oxygen levels have been depleted. With increased productivity, the reservoir would become more eutrophic and the period of anoxia would be extended, leading to more intense internal loading.

While both reservoirs have the potential for internal loading, this study suggests that hypolimnetic aeration could be an effective solution in the future. Despite the difference in scale of the internal loading between the two reservoirs, phosphate and ammonia concentrations declined to levels either very near detectable limits or below.

Conclusion

Since the use of aeration was successful in reducing internal loading in this study, hypolimnetic aeration could be suggested as a solution to internal loading in the Crystal Springs reservoirs. The lower reservoir has demonstrated internal loading as well as periods of anoxia, which could lead to water quality problems for the city of San Francisco. While

the hypolimnion of the upper reservoir is not anoxic and thus does not exhibit internal loading, the potential does exist with increased productivity caused by increased nitrogen loading from chloramine sanitation. Internal loading in the lower reservoir could also become more intense after chloramine sanitation, especially if the system is nitrogen limited. Hypolimnetic aeration has the potential to solve future water quality problems in the reservoir by eliminating internal nutrient loading in the sediment/water interface.

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