EVALUATION OF CALCIUM TREATMENT FOR CONTROL OF PHOSPHORUS IN LAKE ELSINORE

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Summary

The addition of Ca^{2+} to Lake Elsinore can change quite significantly the chemical conditions of the lake. Laboratory experiments demonstrated that addition of agricultural gypsum, rock gypsum and $CaCl_2$ all lowered equilibrium pH and alkalinity levels, while increasing the dissolved Ca^{2+} concentration. Solution pH decreased linearly with increasing Ca^{2+} dose, from 9.0 with no added Ca^{2+}, to about 8.4 at a dose of 200 mg/L. Alkalinity decreased from 10.5 to about 3.5 meq/L, while dissolved Ca^{2+} levels increased from 20.6 to approximately 100 mg/L over this same dose range. Addition of CaO and $Ca(OH)_2$ had a comparatively small effect on equilibrium chemistry and maintained high pH, high alkalinity and low Ca^{2+} levels in the water. The kinetics of these changes were relatively slow; equilibrium was generally reached between 4-7 days depending upon Ca-salt used and the rate of mixing. The Ca-salt additions resulted in modest (30-40%) reductions in total phosphorus (TP) and chlorophyll levels. Sorption and core-flux experiments demonstrated limited capacity of precipitated $CaCO_3$ to sorb soluble-reactive phosphorus (SRP). Significant removal was achieved, however, via coprecipitation of SRP with $CaCO_3$ formed from Ca^{2+}-amended recycled water added to Lake Elsinore water. Based on the results of the study, a lake-wide application of Ca^{2+} is not recommended given the current conditions of the lake (*i.e.*, relatively high TP, low SRP). Treatment of the recycled water stream with agricultural gypsum or other neutral Ca-salt prior to its entering the lake is encouraged, however. Addition of Ca^{2+} to the lake would also be encouraged when high concentrations of SRP are found, for example, following heavy runoff events.

Introduction

Lake Elsinore is subject to high rates of internal loading of P (Anderson, 2001). Geochemical factors limit the effectiveness of aeration and alum, two of the most common in-lake methods for controlling P release, however (Anderson, 2001; Anderson, 2002). High levels of HS^- within the sediment pore water result in precipitation of FeS_2

and very low Fe^{2+} pore water concentrations, thereby restricting the formation of reactive Fe(III) oxyhydroxides near the sediment-water interface. In the absence of such highly sorptive phases, soluble-reactive P is released from the sediments at a rapid rate under both oxic and anoxic conditions. As a result, aeration or oxygenation may only partially curb internal loading of P (Anderson, 2001). Application of alum was explored as an alternative treatment; hydrolysis of alum yields $Al(OH)_3$, a reactive hydroxide phase with a high affinity for P. However, it was shown that the high alkalinity of Lake Elsinore (>10 meq/L) buffered the lake against pH decreases associated with Al^{3+} hydrolysis. Even free-acid formulations were unable to drive the pH down significantly enough to maintain low dissolved Al concentrations (Anderson, 2002).

While the chemistry of the lake was not well-suited for alum application, the chemistry is quite favorable for a Ca treatment and precipitation of $CaCO_3$ (Prepas, 2002) An initial study on the efficacy of CaO addition on P removal and changes in water chemistry in Lake Elsinore was conducted by Viencek and Anderson (1997). Calcium oxide additions from 50-200 mg/L as Ca^{2+} resulted in a linear decrease in SRP and linear increase in pH. Addition of CaO to 200 mg/L Ca^{2+} lowered SRP concentration by >50%, but increased pH from 9 to about 10.6. It should be noted that the alkalinity was lower than that currently found in the lake, however. More recently, $CaCO_3$ formed from $CaCl_2$ addition was found to reduce by 67-88% the flux of SRP from intact cores depending upon aeration status (Anderson, 2000), and to lower the pH and alkalinity of lake water (Anderson, 2002).

The objectives of the proposed study are to more carefully quantify the impacts of varying Ca^{2+} dose and Ca source (*e.g.*, CaO, $CaCl_2$, agricultural gypsum, etc.) on pH, alkalinity, dissolved and total P in the water column and to further evaluate the effectiveness of $CaCO_3$ in controlling SRP release from bottom sediments.

Experimental Approach

A series of experiments were conducted to evaluate the changes in water and sediment chemistry resulting from Ca treatment.

Kinetics of Calcium Carbonate Precipitation and Approach to Equilibrium

In the initial experiment, duplicate sets of five 1-L samples of Lake Elsinore water in plastic beakers were dosed with 200 mg/L Ca^{2+} from one of 5 Ca^{2+} sources: $Ca(OH)_2$, CaO, $CaCl_2$, and two grades of $CaSO_4 \cdot 2H_2O$ (agricultural gypsum and 0.05 – 0.1 mm diameter rock gypsum). Geochemical calculations indicate that, even at this high dose, Ca^{2+} concentrations will remain below the solubility limit for gypsum ($CaSO_4 \cdot 2H_2O$); thus all gypsum should readily dissolve upon addition. One set of samples was vigorously mixed by stirring and aeration, while the 2nd set was very slowly mixed to more closely reflect mixing conditions in the lake. Samples were analyzed over time for pH, alkalinity, electrical conductance, dissolved Ca^{2+}, SRP, TP and TN.

Calcium Dose and Equilibrium Water Chemistry

Following this initial evaluation, a series of batch tests were performed to evaluate the effects of varying Ca^{2+} dose and Ca^{2+} source on equilibrium water column chemistry. Five different Ca^{2+} doses (0, 25, 50, 100, and 200 mg/L) and the 5 different sources were evaluated. Samples were collected and analyzed for the above properties after equilibrium was reached (as determined in kinetics experiment described above).

Phosphorus Sorption to $CaCO_3$

As indicated in the introduction, preliminary work conducted with $CaCO_3$ formed from $CaCl_2$ showed that $CaCO_3$ has some capacity to retain P released from bottom sediments, lowering the P flux rate from Lake Elsinore sediment by 67-88 % relative to untreated cores over approximately a 1-week period. The long-term capacity for $CaCO_3$ to serve as a chemical barrier to P release is not well understood, however. This long-term capacity was evaluated through sorption experiments. Sediment pore water was extracted and analyzed for pH, alkalinity, SRP, and NH_4-N. A known volume of pore water was mixed with an equivalent volume of lake water to which was then added varying amounts of precipitated $CaCO_3$ formed from precipitation via Ca^{2+} addition from $Ca(OH)_2$. In this way, sorption isotherms can be developed under constant initial SRP and DOC (known to inhibit P sorption to $CaCO_3$), mimicking in some ways a steady state SRP (and DOC) flux from the sediments. SRP flux rates combined with sorption data and $CaCO_3$ surface doses will then be used to estimate the expected lifetime of $CaCO_3$ as a chemical barrier to P release from sediments.

Phosphorus Release from Sediments

A core-flux experiment was conducted to test of the use of sorption data from Experiment 3 to estimate the long-term capacity of $CaCO_3$ to serve as a chemical barrier to P release. Eight replicated cores from the deepest part of the lake were collected on

June 11, 2002 and returned to the lab. 1.7 g of $CaCO_3$ precipitated from Lake Elsinore water via $Ca(OH)_2$ addition at a rate of 200 mg Ca^{2+}/L was added to 3 of the intact cores. This mass provided a uniform layer on the sediments approximately 1-2 mm thick, equivalent to 537 g $CaCO_3/m^2$. Dissolved P was then monitored in the overlying water for the following 10 days.

Results

Kinetics of Calcium Carbonate Precipitation and Approach to Equilibrium

The chemistry of Lake Elsinore water changed quite dramatically following addition of Ca from the different sources. For example, pH decreased from an initial value of 9.0 to about 8.2 after 20 min following addition of 200 mg Ca^{2+}/L as agricultural gypsum, rock gypsum and $CaCl_2$ (neutral salts), while pH initially increased to pH 10.0-10.3 after treatment with CaO and $Ca(OH)_2$ salts (Fig. 1).

The pH of the neutral salt-treated water increased slightly over the next several days to reach an equilibrium value of about 8.4, while pH returned to about 9 for water with added basic (CaO and $Ca(OH)_2$) salts (Fig. 1). The pH declined relatively rapidly for the $Ca(OH)_2$ solution, dropping below 10 after about 3 h and below 9.4 after 1 day. The pH of the CaO-treated water decreased more slowly, dropping to 9.5 after only 4 days (Fig. 1). These findings indicate a rather slow approach to equilibrium for the solutions.

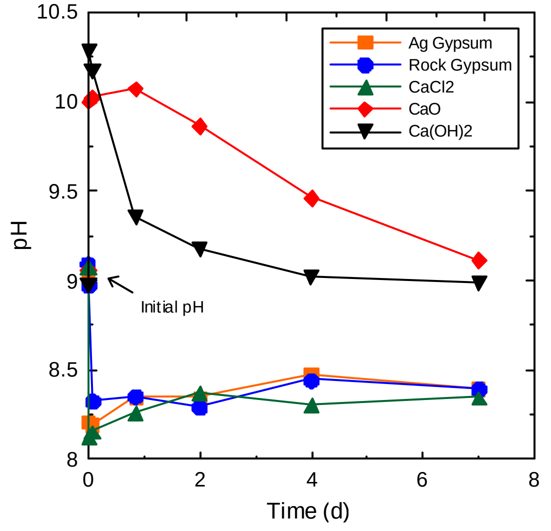

Fig. 1. pH over time following addition of 200 mg/L Ca^{2+} from 5 different salts.

Total alkalinity of the various Ca-treated lake waters also showed significant differences for the different Ca-sources and over time (Fig. 2). Alkalinity declined from an initial value of 10.5 meq/L for the untreated water to an equilibrium value of about 3.5 meq/L, corresponding to a loss of 7 meq/L alkalinity following addition of the three neutral Ca-salts. Alkalinity of the agricultural gypsum and $CaCl_2$-treated waters tracked each other quite closely and approached their equilibrium value after about 2 days, while rock gypsum lost alkalinity more slowly (Fig. 2). Alkalinity loss for these waters results

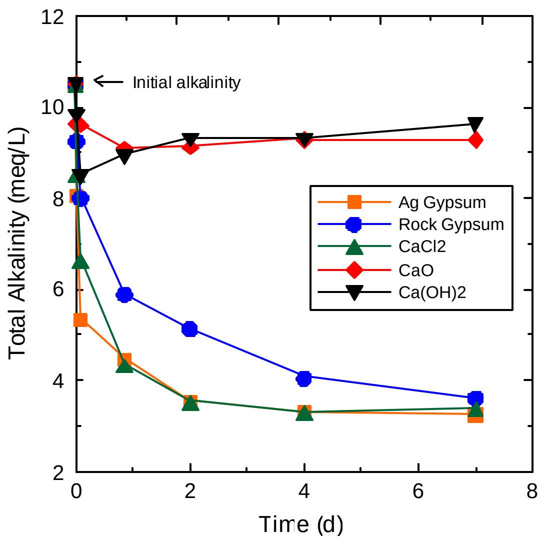

Fig. 2. Total alkalinity over time following addition of 200 mg/L Ca^{2+} from 5 different salts.

from the precipitation of calcium carbonate (as calcite or aragonite) by the reaction (eq 1):

$$Ca^{2+} + 2HCO_3^- \text{ « } CaCO_3 + CO_2 + H_2O$$

The formation of $CaCO_3$ removes 2 equivalents of alkalinity and 1 mole of Ca^{2+} for each mole of $CaCO_3$ formed. Total alkalinity (as sum of bicarbonate+carbonate+OH^-) for the basic salts decreased only modestly (about 1 meq/L, from 10.5 to 9.5 meq/L) due to the addition of free hydroxyls for $Ca(OH)_2$, and due to hydrolysis of CaO by the reaction:

$$CaO + H_2O \text{ ® } Ca^{2+} + 2OH^- \qquad (2)$$

For these waters, alkalinity dominated by bicarbonate at the lake pH (calculated 93% HCO_3^-, 7% as CO_3^{2-}) is replaced by the carbonate species by the reaction:

$$HCO_3^- + OH^- \text{ ® } CO_3^{2-} + H_2O \qquad (3)$$

Dissolved Ca^{2+} concentrations were substantially higher following addition of the neutral Ca-salts as compared to the native lake water and lake water treated with 200 mg/L Ca from the basic salts (Fig. 3). The Ca^{2+} concentration in Lake Elsinore is 20.6 mg/L. Addition of agricultural gypsum and $CaCl_2$ yielded dissolved Ca^{2+} levels of about 200 mg/L after 20 min, which then declined over the next several days to reach an equilibrium concentration of 80-90 mg/L (Fig. 3). Rock gypsum apparently dissolved somewhat less rapidly than agricultural gypsum, reaching a maximum dissolved level of about 160 mg/L, although did also reach an equilibrium concentration of about 90 mg/L at the end

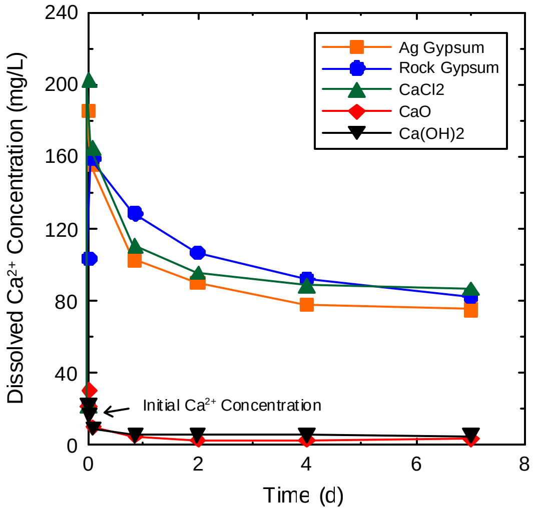

Fig. 3. Dissolved Ca^{2+} concentrations over time following addition of 200 mg/L Ca^{2+} from 5 different salts.

of the experiment (Fig. 3). The basic Ca-salts (CaO and $Ca(OH)_2$) yielded a slight increase in dissolved Ca^{2+} immediately after salt addition, but rapidly reached very low levels in solution (Fig. 3).

It is instructive to compare the Ca^{2+} lost from solution with the observed alkalinity levels in the different waters. The neutral Ca-salts yielded an equilibrium Ca^{2+} level of about 80 mg/L representing a loss of approximately 140 mg/L (20 mg/L native Ca^{2+} + 200 mg/L Ca-salt – 80 mg/L remaining) or 3.5 mmol Ca^{2+}. As noted in eq 1, 2 equivalents of alkalinity are lost for each mole of Ca^{2+}, so one estimates a loss of 7.0 meq/L of alkalinity associated with this Ca^{2+} loss. This is in complete accord with measured loss of alkalinity of 7.0 meq/L (Fig. 2). Thus it appears that all of the added gypsum was dissolved into the water or converted to $CaCO_3$ by the end of the experiment.

Similar calculations for the basic Ca-salts point to little net loss of alkalinity from solution. That is, addition of the equivalent of 10 mmol OH^-/L converts effectively all of the HCO_3^- species to CO_3^{2-}, effectively doubling the total alkalinity of the system (~20 meq/L) and raising only modestly the pH. (For comparison, 10 mmol/L OH^- added to an unbuffered solution is predicted to increase the pH to 12.) Reaction of Ca^{2+} with CO_3^{2-} removes 2 eq/L alkalinity per mol of Ca^{2+}, so loss of ~210 mg/L Ca^{2+} corresponds to a loss of 10.5 meq/L alkalinity to yield a final alkalinity slightly below 10 meq/L. Importantly then, addition of $Ca(OH)_2$ or CaO does not raise the equilibrium $Ca:HCO_3^-$ ratio.

The dependence of the rate of $CaCO_3$ precipitation and approach to chemical equilibria on the rate of mixing was also evaluated. Relatively rapid mixing (results presented in Figs. 1-3) hastened the approach to equilibrium relative to weakly mixed waters, although all waters approached equilibrium within about 7 days (data not shown).

Calcium Dose and Equilibrium Water Chemistry

The previously described experiment indicated that equilibrium was reached after 4-7 days, depending upon Ca-salt used. Thus, different doses of the various Ca-salts were allowed to equilibrate for 7 days prior to filtering and analysis.

As indicated in the prior section, the equilibrium chemistry varied strongly depending upon Ca-salt used, with the magnitude of the changes a function of the amount of Ca^{2+} added (*e.g.*, Fig. 4). Equilibrium pH for the neutral Ca-salts decreased linearly with increasing Ca^{2+} dose, while the pH for the basic Ca-salts remained near the native pH value of 9 (Fig. 4).

The total alkalinity of the waters also varied as a function of type of Ca salt and the Ca^{2+} dose (Fig. 5). Alkalinity decreased with increasing Ca^{2+} dose, although in a non-linear way with dose when compared with the trend with pH. As previously noted in Fig. 2, total alkalinity decreased substantially for the neutral salts, with little decrease in alkalinity observed for the basic Ca-salts. The total alkalinities were quite similar for the 3 different neutral Ca-salts (agricultural gypsum, rock gypsum and $CaCl_2$), suggesting little difference between these salts and their ability to precipitate $CaCO_3$.

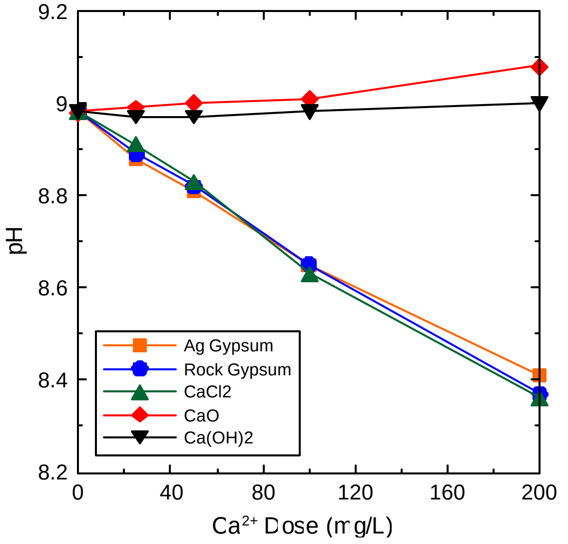

Fig. 4. Equilibrium pH as a function of Ca^{2+} dose for the 5 different salts.

Dissolved Ca^{2+} concentrations increased with increasing Ca dose for the neutral Ca-salts, from the native level of 20.6 mg/L to 100 – 110 mg/L at the highest (200 mg/L) dose (Fig. 6). The nonlinear (upward) increase in the slope of the dissolved-dose plots indicates that less Ca^{2+} is being sequestered as $CaCO_3$ at the higher doses. This would be expected given the pH-dependence of $CaCO_3$ solubility (*i.e.*, increased solubility with decreased pH as shown in Fig. 4). Dissolved Ca^{2+} decreased with increased Ca^{2+} dose from basic Ca-salts (CaO and $Ca(OH)_2$) (Fig. 6); that is, all added Ca^{2+} is being precipitated as $CaCO_3$ (along with some native Ca^{2+}).

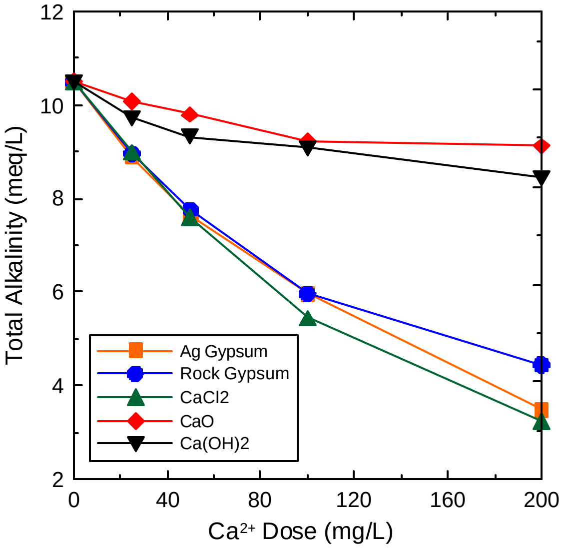

Fig. 5. Total alkalinity as a function of Ca^{2+} dose for the 5 different salts.

Electrical conductance and TDS levels varied only modestly across the different treatments. The neutral salts increased slightly the EC and TDS levels relative to the native lake water (*e.g.*, the highest TDS was associated with 200 mg/L dose of $CaCl_2$ at 1934 mg/L as compared with 1680 mg/L for unamended lake water). Conversely, the basic Ca-salts actually lowered somewhat the EC and TDS (e.g., a TDS of 1537 mg/L was measured for the highest $Ca(OH)_2$ dose).

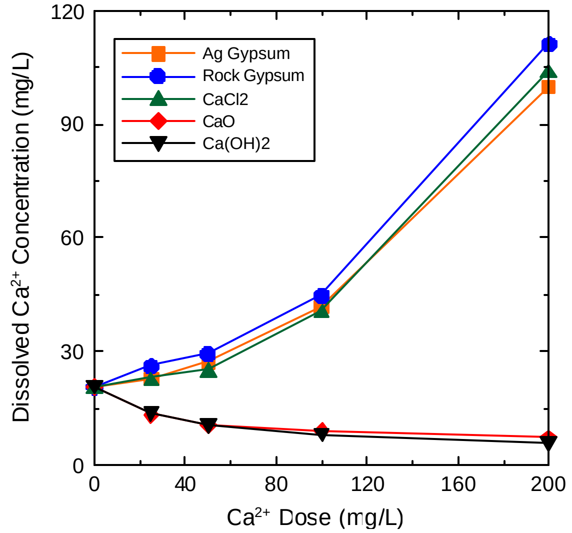

Fig. 6. Dissolved Ca^{2+} concentration as a function of Ca^{2+} dose for the 5 different salts.

As previously noted, Lake Elsinore has a very low $Ca:HCO_3^-$ ratio (about 0.1 when expressed in eq/L) that, with recent evapoconcentration, has resulted in the lake evolving into a relatively high pH, sodic, high alkalinity water. Continued evaporation concentrates all ions in solution and promotes precipitation of $CaCO_3$. Since the $Ca:HCO_3^-$ ratio is less than 1, the excess alkalinity maintains low dissolved Ca^{2+} levels in the lake. Increased evaporation would further drive Ca^{2+} levels lower while alkalinity would continue to increase. Using the data from Figs. 5 and 6, one calculates the equilibrium $Ca:HCO_3^-$ ratio increased from 0.10 to 0.13, 0.18, 0.35 and 1.43 for the 0, 25, 50 100, and 200 mg/L Ca doses, respectively, for the neutral Ca-salts. Thus, a dose of somewhat less than 200 mg/L is required to switch Lake Elsinore to the other side of the chemical divide, wherein continued evaporation would yield a moderate pH, low alkalinity water.

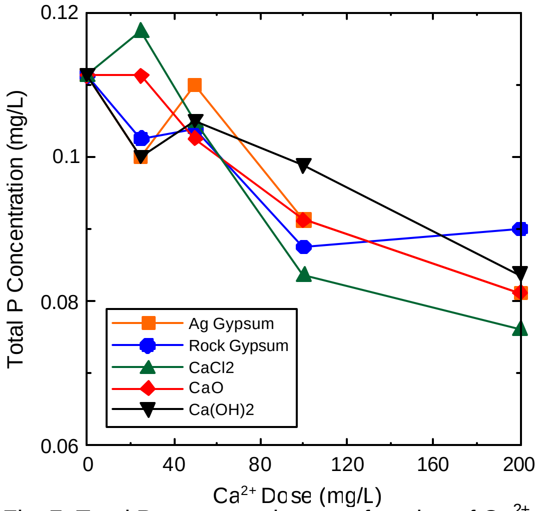

Fig. 7. Total P concentration as a function of Ca^{2+} dose for the 5 different salts.

The addition of Ca^{2+} yielded modest reductions in total P (Fig. 7) and chlorophyll (Fig. 8). Total P concentrations in the lake water averaged 0.110 mg/L; concentrations decreased approximately linearly with Ca^{2+} dose to yield an average value near 0.08 mg/L (or 27% reduction) at the highest dose (Fig. 7). The reduction in TP appeared to be fairly similar across the different sources, although there was significant scatter in the data.

Chlorophyll a levels in the waters showed similar trends as total P. That is, although quite a bit of scatter in the data was found, there was a general relatively modest decrease in chlorophyll a concentrations with increasing Ca^{2+} dose, irrespective of the particular Ca-salt used (Fig. 8). The reductions in chlorophyll a level were somewhat higher than total P, however (~40%). Similar trends were found for turbidity, although because of scattering by colloidal $CaCO_3$, somewhat greater variability was found (data not shown).

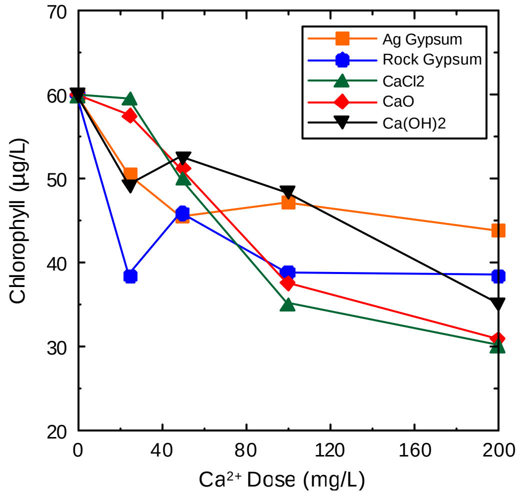

Fig. 8. Chlorophyll concentration as a function of Ca^{2+} dose for the 5 different salts.

Since recycled water will be added to Lake Elsinore to help offset evaporative losses, the chemical changes resulting from recycled water addition were also quantified. The basic chemical parameters of lake water, recycled water obtained from the Elsinore Valley Municipal Water District regional treatment plant, and lake water samples augmented with 10% and 30% recycled water are summarized in Table 1. The water quality changes resulting from addition of a 200 mg/L Ca^{2+} dose, as agricultural gypsum or $Ca(OH)_2$, to a 70:30 mix of lake water:recycled water were also evaluated in equilibrium batch experiments as described above (Table 1).

The recycled water bore a lower pH, TDS and alkalinity but higher Ca^{2+} and much higher TP and SRP levels than the receiving lake water (Table 1). The higher Ca^{2+} concentration of the recycled water may result in some precipitation of calcium carbonate; assuming a conservative 2-member mixing model, one expects alkalinities of 9.7 and 8.2 meq/L for the 10 and 30% recycled water mixtures, respectively. This compares with measured values of 9.3 and 7.8 meq/L, about 5% lower than the predicted conservative values. Calcium levels in the recycled water mixtures were also slightly lower than the ideal concentrations predicted assuming conservative behavior (Table 1). Thus it may be that recycled water addition resulted in some limited $CaCO_3$

precipitation, although analytical variability may also be responsible for the observed differences.

Table 1. Water quality properties of selected waters.

Sample	pH	TDS (mg/L)	Alkalinity (meq/L)	Ca^{2+} (mg/L)	TP (mg/L)	SRP (mg/L)
Lake Elsinore	9.01	1591	10.5	20.6	0.111	0.005
Recycled Water (RW)	7.65	577	2.8	56.7	2.561	2.591
10% RW[a]	8.95	1530	9.3	22.9	0.339	0.201
30% RW[a]	8.90	1352	7.8	30.7	0.846	0.698
30% RW + 200[a] mg/L $Ca(OH)_2$	8.90	1257	6.8	na	na	0.115
30% RW+ 200[a] mg/L Ag Gypsum	8.34	1527	4.1	na	na	0.061

[a] values reflect properties at equilibrium (after 7 d equilibration)

Of particular interest is the fate of phosphorus in mixtures of lake water and recycled water, both alone and when dosed with Ca^{2+}. Total P levels are in line with mixing calculations as expected (*e.g.*, the measured TP concentration for 10% RW of 0.339 mg/L is within 5% of the predicted concentration of 0.356 mg/L). In comparison, SRP *was* lost from solution (*e.g.*, at 10% RW, the 2-member mixing model, using the SRP values from Table 1, points to an SRP concentration of 0.264 mg/L, while only 0.201 mg/L was actually measured, representing a loss of 24%). Slightly higher loss of SRP was found for the 30% RW treatment.

Addition of 200 mg/L Ca^{2+} as $Ca(OH)_2$ or agricultural gypsum lowered substantially the SRP levels in 30% RW solutions relative to untreated waters (Table 1). Agricultural gypsum lowered the SRP level by more than 90% (from 0.698 to 0.061 mg/L), while $Ca(OH)_2$ lowered the SRP concentration by 84% (to 0.115 mg/L).

Phosphorus Sorption to $CaCO_3$

The potential for $CaCO_3$ formed in the water column to sorb soluble-reactive phosphorus (SRP) released from the sediments was evaluated through a sorption experiment. The results of the experiment are shown in Fig. 9. The $CaCO_3$ had some capacity to retain SRP, sorbing up to about 0.5 mg SRP/g $CaCO_3$ at equilibrium solution concentrations of 2 - 2.5 mg/L. The sorption data conformed reasonably well to both the Freundlich and Langmuir adsorption models (R^2=0.94 and 0.97, respectively). The fitted

Langmuir model is shown in Fig. 9. The fitted Langmuir model yielded a sorption maximum of 2.25 mg P/g $CaCO_3$, although very high equilibrium solution concentrations would be necessary to fully saturate all reactive sites. At the SRP concentrations near the sediment-water interface (est. 0.10 - 0.30 mg/L), one would expect 0.035 – 0.102 mg SRP/g $CaCO_3$ (Fig. 9).These sorption data are in reasonable accord with other published studies on P sorption to $CaCO_3$ (*e.g.*, Freeman and Rowell, 1981) as well as work conducted here at UCR, and point to rather limited capacity to retain P.

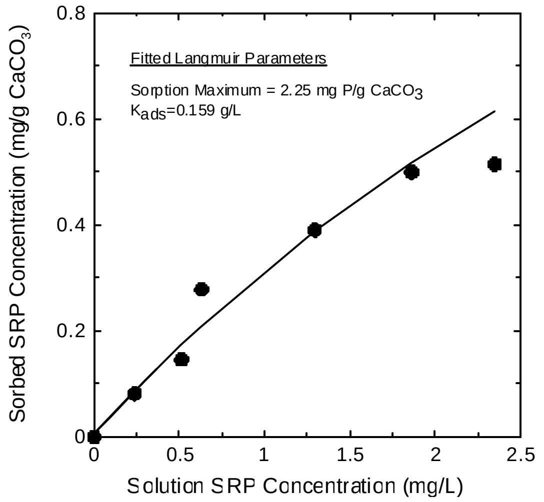

Fig. 9. SRP sorption isotherm for $CaCO_3$. Line represents fitted Langmuir model.

Phosphorus Release from Sediments

The flux of SRP from intact cores was measured for triplicated cores maintained at the temperature and DO level found at the time of sampling (~22 °C and ~2 mg/L, respectively), and from cores to which $CaCO_3$ was added at a rate equivalent to 537 g $CaCO_3$/m^2 (or 215 g Ca^{2+}/m^2) of sediment (Fig. 10).

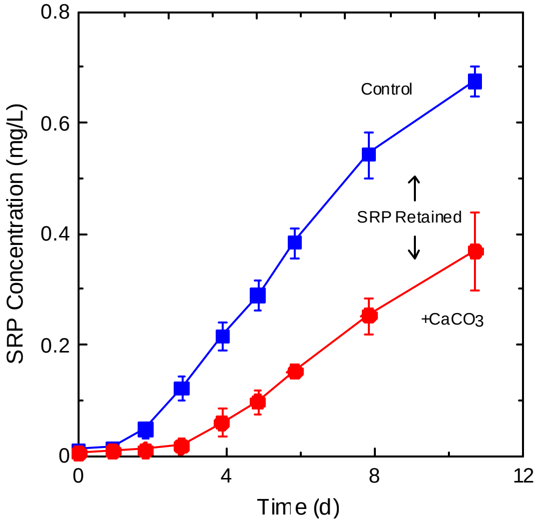

Fig. 10. SRP concentration over time from core-flux experiment.

The concentration of SRP in the overlying water remained relatively constant at very low levels for both the control cores and the cores treated with $CaCO_3$ over the first day following sampling. Following this initial phase, the concentration of SRP in the overlying water of the control cores increased linearly with increasing time out to 8 days (Fig. 10). The rate of SRP release decreased slightly over the 8 – 10.7 day time interval, presumably due to the loss of mineralizable organic matter at longer times. The isolation of the sediment from the water column eliminates the delivery of fresh particulate material to the sediment surface. The linear portion of the plot in Fig. 10 was used to calculate an SRP flux rate of 12.9 $mg/m^2/d$ (Table 2). The concentration of SRP in the water overlying the $CaCO_3$-treated cores showed negligible increases over the first 2 days, with measurable but still modest increases found only after 2.8 days. The SRP levels in water overlying the sediments treated with $CaCO_3$ then increased linearly; these concentrations were used to calculate a flux rate approximately one-half of that found in the control cores (Table 2).

The delay in appearance of SRP in the overlying water and the reduced concentration at any given time relative to the control cores results from sorption of SRP onto the $CaCO_3$ deposited onto the sediment surface. Assuming the flux from the actual sediment surface is unchanged by addition of the $CaCO_3$ layer, the difference between the 2 curves can be used to calculate the mass of SRP retained by the $CaCO_3$; for example, after 4.8 days the $CaCO_3$ retained 99.1 µg or 67% of the SRP released from the sediments. At a $CaCO_3$ mass of 1.70 g added to each of the treated cores, this corresponds to 0.058 mg SRP/g $CaCO_3$. After 10.7 days, the $CaCO_3$ layer retained 0.179 mg SRP/g $CaCO_3$.

Since diffusion through the 1-2 mm thick $CaCO_3$ layer should be relatively rapid (est. 15-30 min diffusion time), mineralization of the surficial material and/or release from the sediment body can be considered rate-limiting. As a result, a strong concentration gradient within the $CaCO_3$ layer is not expected. Thus, it seems reasonable to assume that the $CaCO_3$ is in equilibrium with the overlying water. Using the Langmuir model previously developed, one can independently estimate the sorbed concentration of P on the $CaCO_3$. At an equilibrium SRP solution concentration of 0.097 ± 0.023 mg/L, one estimates an equilibrium sorbed P content of 0.034 ± 0.008 mg P/g $CaCO_3$, a value that is about 40% less than the measured value (0.058 mg P/g $CaCO_3$). After 10.7 days, an average solution concentration of 0.369 ± 0.069 mg/L was found in the overlying water (Fig. 10); inserting this value into the Langmuir model yields a predicted sorbed concentration of 0.125 mg P/g $CaCO_3$, a value that is 30% below the measured value of 0.179 mg P/g $CaCO_3$. Thus it appears that SRP is retained by $CaCO_3$ in the cores beyond that predicted using the sorption isotherm data. Additional data points collected at lower concentrations during the sorption experiments would probably improve the predictive capability of the model at lower SRP levels.

SRP flux was also determined on a single core that was actively aerated to maintain a DO level near 8 mg/L, and on an additional core that was purged with N_2 (DO <1 mg/L). The rate of flux for the N_2-purged core (DO <1 mg/L) and the control cores (DO ~1-2 mg/L) were comparable, indicating that strongly reducing conditions did not hasten SRP flux from the sediments relative to the low DO conditions found near the sediments at the time of sampling. Consistent with previous measurements, aeration had only a moderate effect on SRP flux, reducing it about 30% from 12.9 to 8.7 mg/m^2/d (Table 2). It bears noting that the sediment samples as retrieved from the lake had patchy surface films of *Beggiatoa* (a sulfur-oxidizer) that were maintained in the control cores. These bacterial films were more extensively developed on the N_2-purged core surface, and absent in the aerated core. In its place, a thin (~1-2 mm) light brown layer overlaid the greenish-black sediments found deeper in the aerated (and other) core(s). Nevertheless, this layer did not significantly impede SRP release over the duration of the experiment. Moreover, such a layer has not been observed by the author in any sediment cores or grab samples collected from the lake (under oxic or anoxic conditions). This may be due to the high rate of sedimentation and deposition of fresh detrital material and resuspended material in Lake Elsinore (Anderson, 2001).

Table 2. SRP flux measured in core-flux experiment.

Treatment	**SRP Flux (mg/m2/d)**
Control (n=3)	12.9 ± 0.7
$CaCO_3$ (n=3)	6.3 ± 0.3
Aerated	8.7 ± na
N_2-Purged	10.5 ± na

Discussion and Conclusions

Calcium addition has the potential to change quite substantively the chemistry of Lake Elsinore. Addition of neutral salts (agricultural gypsum, rock gypsum or $CaCl_2$) will lower the equilibrium pH and alkalinity while raising the residual Ca^{2+} level. The extent of these changes vary with the Ca^{2+} dose applied. Addition of basic Ca-salts, such as $Ca(OH)_2$ and CaO, were found to have limited effects on the equilibrium chemistry, however, yielding pH, alkalinity and Ca^{2+} levels broadly comparable to the levels found in the lake samples prior to treatment. Electrical conductance and TDS levels varied only modestly across the different treatments. Total P and chlorophyll a concentrations both decreased fairly uniformly with increasing Ca^{2+} dose, without a clear difference between the different Ca-salts. Total P was lowered from 0.111 mg/L in the native lake water to about 0.08 mg/L at the highest Ca^{2+} dose, while chlorophyll a levels decreased from 60 to 35 - 40 µg/L.

The above observations are important for a number of reasons. First of all, Ca^{2+} additions had a modest effect on the TP and chlorophyll levels in lake water. Thus, a marked clearing of the water following Ca^{2+} treatment does not appear likely. Secondly, the precipitated $CaCO_3$ has a low affinity for SRP relative to $Al(OH)_3$ and other more reactive solid phases. As a result, precipitated $CaCO_3$ offers limited impedance to SRP flux from the sediments, with the extent of sorption apparently related to the equilibrium SRP concentration in the overlying water column. Thus, low water column SRP levels will result in low sorption efficiency. This low sorptive efficiency was manifested in core-flux measurements. At an areal dose equivalent to 537 g $CaCO_3/m^2$ (equivalent to an average volumetric dose for the mean depth of the lake equal to about 50 mg Ca^{2+}/L), $CaCO_3$ reduced the average flux rate from 12.9±0.7 to 6.3±0.3 mg $SRP/m^2/d$.

Calcium additions concurrent with recycled water resulted in coprecipitation reactions that were more effective at sequestering SRP than sorption to precipitated $CaCO_3$. The data in Table 1 indicate that 1.2 – 3.4 mg SRP/g $CaCO_3$ was coprecipitated with $CaCO_3$ formed in the presence of both recycled water and lake water. This level of retention is markedly higher than the levels found during sorption experiments (0.02 – 0.04 mg SRP/g $CaCO_3$) at these low (0.061 – 0.115 mg/L) equilibrium solution levels. This level of removal is also much higher than that found for TP (0.05 – 0.1 mg TP/g $CaCO_3$). Thus, per unit mass of Ca^{2+} added, coprecipitation of SRP with $CaCO_3$ is greater than 10x more effective than precipitation and flocculation of TP or sorption of SRP to the $CaCO_3$ surface.

It is useful to also point out that the $Ca:HCO_3^-$ ratio of the recycled water is right at 1.0 (Table 1), so recycled water can not shift the $Ca:HCO_3^-$ ratio of the lake above 1.0. Moreover, runoff can often bears a $Ca:HCO_3^-$ ratio less than or approximately equal to 1 (*e.g.*, Canyon Lake $Ca:HCO_3^-$ ratio is approximately 1.1), so Ca^{2+} additions (from neutral Ca-salts) sufficient to shift the ratio >1 for the lake (at a dose near 200 mg Ca^{2+}/L) will not necessarily offer long-term chemical protection against the return of high pH, high alkalinity conditions to the lake. As previously noted, addition of basic Ca-salts (CaO or $Ca(OH)_2$) do not consume alkalinity and are not recommended for this lake.

In light of the above considerations, treatment of the lake under the current conditions (*i.e.*, relatively high TP, low SRP) is not recommended. Calcium addition to the lake will be much more effective during periods of high SRP concentrations (*e.g.*, during heavy runoff events). Calcium input into the recycled water stream prior to discharge into the lake will also maximize P removal per unit mass of Ca^{2+} added. Depending upon the transit time in the drainage channel, agricultural gypsum added at the treatment plant effluent should be the most cost-effective form of Ca used for this application, although simple field tests should be conducted to confirm and optimize performance.

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