

IMPACTS OF ALUM ADDITION ON WATER QUALITY IN LAKE ELSINORE

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Summary

A series of studies were conducted to evaluate the impacts of alum addition on water quality in Lake Elsinore. As an initial step, sediment characterization and nutrient flux data were used to identify the alum treatment area within the lake. Fine organic ("type III") and transitional ("type II") sediments were previously identified as contributing as much as 95% of the soluble-reactive phosphorus (SRP) flux to the water column, while shallow, coarse-textured sediments contributed relatively little (Anderson, 2001). The total area requiring treatment corresponded to 2250 acres (1440 and 810 acres of type III and type II sediments, respectively). Following Cooke (2001), the proposed dose of 48 g Al/m² was used in conjunction with the proposed treatment area (2250 acres or 9.1×10^6 m²), and a volume at 1240' elevation of 47.5×10^6 m³ to estimate an equivalent water column Al concentration of 9.2 mg/L. This dose, as well as higher (13 and 18 mg/L) doses, was used in subsequent laboratory studies that quantified the changes in water chemistry resulting from alum and high-acid alum treatment.

The high alkalinity in the lake limited the capacity for alum at the 9.2 mg/L Al dose to reduce the equilibrium pH below 8.7. High acid alum formulations and higher Al doses were somewhat more successful at lowering the pH, however. For example, Al doses of 9.2 mg/L+20% H₂SO₄ and 18 mg/L (no free acid) were able to lower the pH to approximately 8.5. The highest dose and free-acid content (18 mg/L+20% H₂SO₄) was most effective, lowering the pH to about 8. Dissolved Al concentrations varied strongly as a function of Al dose, percent free acid in the high-acid alum formulations, and time. Dissolved Al concentrations increased with increasing pH, and approached (or exceeded) 2 mg/L in some samples, although they remained below predicted levels based on solubility of amorphous Al(OH)₃. pH and dissolved Al concentrations both varied markedly over time, however, due to kinetic limitations to CO₂ outgassing and other reactions. Dissolved Al concentrations monitored in longer-term core experiments decreased over time, suggesting transformation of amorphous, high-solubility Al phase(s) to more crystalline, lower-solubility phases. Changes in water quality from Ca²⁺ addition to Lake Elsinore were also evaluated.

Introduction

Alum has been used extensively as a reactive barrier to control internal loading of phosphorus (P) in lakes. An alum treatment has been proposed for P control in Lake Elsinore, although a number of questions have been raised about its potential impacts on water quality. In light of this, a series of studies have been conducted to better understand the nature and extent of water quality changes resulting from alum addition to the lake. Specifically, studies were conducted to:

- (1) Estimate the alum treatment area based upon sediment characterization data and calculate the appropriate alum dose to the water column assuming 48 g Al/m²/d.
- (2) Evaluate the change in pH, alkalinity, dissolved aluminum (Al) concentration and other water quality parameters following alum and high acid alum additions at the prescribed alum dose.
- (3) Quantify the potential for resolubilization of alum floc assuming the lake's ambient pH returned to previous levels (9-9.5).

1. Alum Treatment Area and Dose Calculations

An extensive characterization of the sediments of Lake Elsinore and their internal loading rates has been recently completed as part of the TMDL development efforts of the Santa Ana Regional Water Quality Control Board (Anderson, 2001). In that study, 49 sediment grab samples were collected across the lake with a Ponar sampler and characterized as to their particle size, CaCO₃ content, organic C, N, S, and total and inorganic P concentrations. Porewater

samples were also collected and analyzed for NH₄-N and soluble-reactive P (SRP) (Anderson, 2001). A graphical cluster analysis demonstrated that 3 distinct types of sediments were found within the lake (Fig. 1): a coarse-textured material found in relatively shallow water that was low in C, N, S and P ("type I"), a fine-organic sediment high in C, N, S and P found in the deeper portions of the lake ("type III"), and a

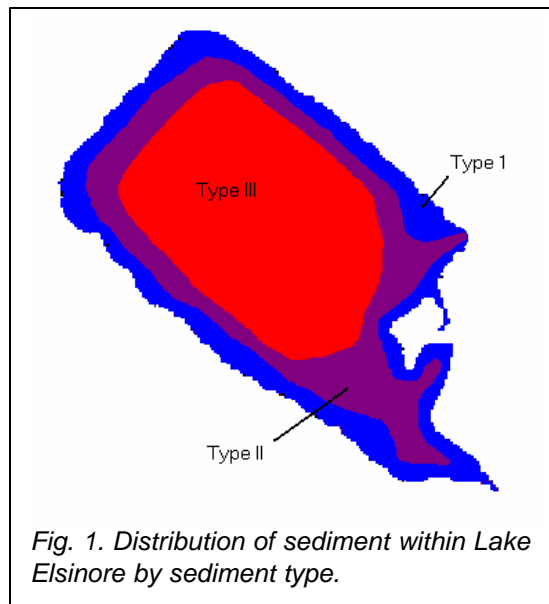


Fig. 1. Distribution of sediment within Lake Elsinore by sediment type.

transitional sediment intermediate in its properties (“type II”). The distribution of these 3 sediment types within Lake Elsinore is shown in Fig. 1. The mean properties associated with each of these sediment types are provided in Table 1.

Table 1. Mean sediment properties by type (Anderson, 2001).

MEAN PROPERTY	Units	Type I	Type II	Type III
Area	acres	750	810	1440
Depth	m	2.8 ± 1.1	4.9 ± 0.9	6.3 ± 0.6
Sand	%	70.8 ± 31.2	29.5 ± 15.4	4.1 ± 4.0
Silt	%	19.7 ± 23.6	48.1 ± 11.9	44.8 ± 6.8
Clay	%	9.5 ± 11.7	22.3 ± 5.4	51.2 ± 6.3
Total C	%	1.07 ± 1.44	3.04 ± 0.86	5.97 ± 0.39
Organic C	%	0.79 ± 1.06	2.13 ± 0.75	4.84 ± 0.45
Inorganic C	%	0.28 ± 0.42	0.90 ± 0.20	1.14 ± 0.26
CaCO ₃	%	2.34 ± 3.46	7.53 ± 1.66	9.5 ± 2.2
Total N	%	0.10 ± 0.12	0.27 ± 0.07	0.53 ± 0.03
Total S	%	0.14 ± 0.30	0.53 ± 0.28	1.18 ± 0.08
Total P	mg/kg	425 ± 209	781 ± 165	916 ± 73
Inorganic P	mg/kg	340 ± 170	595 ± 128	573 ± 77
Organic P	mg/kg	84 ± 97	196 ± 104	342 ± 71
SRP	mg/L	0.6 ± 1.3	3.1 ± 0.6	4.9 ± 1.2
NH ₄ -N	mg/L	6.8 ± 6.9	14.5 ± 6.1	20.0 ± 3.7

Subsequent nutrient release studies found that SRP and NH₄-N flux was considerable from both the type II and type III sediments, such that >95% of the internal loading of SRP was attributed to these two sediment types (13,650 and 18,410 kg/yr, respectively), comprising 2250 acres or 75% of the lake bottom. Thus, it was assumed that this 2250 acres will be targeted for alum treatment. Following Cooke (2001), the proposed dose of 48 g Al/m² was used in conjunction with the proposed treatment area (2250 acres or 9.1 x 10⁶ m²), and a volume at 1240' elevation of 47.5x10⁶ m³ to estimate an equivalent water column Al concentration of 9.2 mg/L.

2. Water Quality Changes Following Alum Addition

The impact of a water column equivalent dose of Al of about 9.2 mg/L was then evaluated. Doses of approximately 13 and 18 mg/L (equivalent to about 70 and 100 g Al/m²) were also investigated in the event that higher doses would be deemed desirable or necessary. As noted by Cooke (2001) and others, the high pH (~9) of Lake Elsinore

presents some special considerations. Specifically, the solubility of Al is known to increase dramatically at high pH values through the formation of the $\text{Al}(\text{OH})_4^-$ (aluminate) species (Stumm and Morgan, 1982). Cooke (2001) proposed use of high acid alum to help lower the pH sufficiently to minimize $\text{Al}(\text{OH})_4^-$ formation. Clar-Ion® alum formulations with sulfuric acid (5, 7, 10 and 20%) were received from Chris Lind (General Chemical). A 15% formulation was prepared by mixing equal parts of 10 and 20% acid alums. For this study, regular alum (0% acid), 5, 10, 15 and 20% acid formulations were used, yielding a 3 x 5 design (3 water column doses x 5 acid levels) for a total of 15 different treatments.

Alum and high-acid alums were added as liquids to known volumes of Lake Elsinore water collected on 16 November 2001. The pH of the water at the time of sampling was 9.05, while temperature and DO values were 18.0 °C and 6.6 mg/L, respectively. pH changes following alum addition were monitored using an Orion pH meter and a Corning gel combination electrode that was regularly standardized against Fisher pH buffers (7.00±0.02 and 10.00±0.02). Alkalinity was measured on samples before and after alum addition by potentiometric titration with standardized acid to an endpoint of 4.5±0.1. Aluminum concentrations were determined colorimetrically using ferron (Bloom and Erich, 1989). Samples were collected for total analysis shortly after alum addition and acidified with Optima trace metals-grade HNO_3 to pH 1.5; dissolved Al was measured on samples filtered through Gelman 0.45 µm filter cartridges that were subsequently acidified. Chlorophyll a was measured on selected samples using an *in vivo* fluorescence method with excitation at 430 nm and emission at 664 nm (AWWA, 1986).

Equilibrium pH values for alum-treated Lake Elsinore water are shown in Fig. 2. As one can see, pH values remained quite high across the various Al doses and acid contents. pH values decreased from about 9.0 prior to alum addition to 8.7 at a dose of about 9.2 mg/L (rounded and labeled 9 mg/L on this and subsequent figures). The pH decreased incrementally with increased free acid, from about 8.7 down to 8.5 at the highest acid dose (20%). Higher Al doses (13 and 18 mg/L) resulted in correspondingly

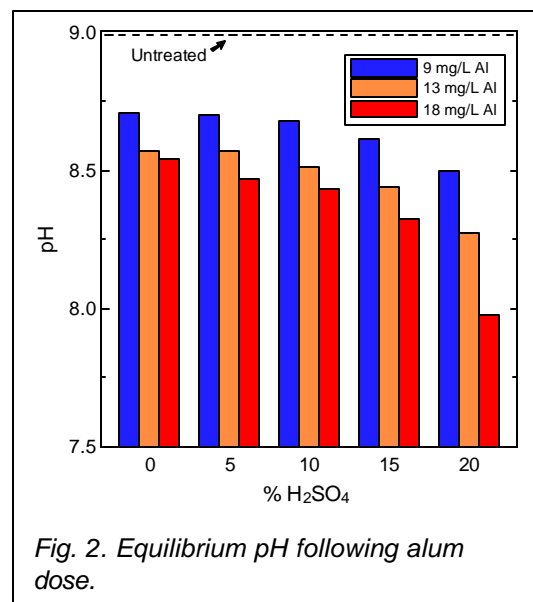


Fig. 2. Equilibrium pH following alum dose.

lower equilibrium pH values. Nevertheless, a dose of alum with 20% H₂SO₄ equivalent to approximately 18 mg Al/L was necessary to decrease the pH below 8.0.

The resistance of the Lake Elsinore water to pH change following acid inputs results from its very high alkalinity. The alkalinity of Lake Elsinore is currently about 9.6 meq/L, or almost 500 mg CaCO₃/L. Note that this is much higher than the lake hardness, which stands at about 200 mg/L CaCO₃. As will be discussed later, the high pH values for Lake Elsinore arise due to the geochemical composition of the water, where Na-HCO₃-Cl – SO₄ dominates the major ion chemistry of the system.

Alkalinity dropped incrementally with alum addition. Hydrolysis of Al³⁺ to form Al(OH)₃ generates significant acidity through the reaction:



Thus approximately 0.11 meq H⁺ are generated for each mg of Al added. If the aluminate species is formed:



then about 0.15 meq H⁺/mg Al are generated.

As one can see in Fig. 3, addition of about 9 mg/L Al decreased the alkalinity by about 1 meq/L (from about 9.6 to 8.6 meq/L), consistent with the above chemical equation (9 mg Al/L * 0.11 meq/mg Al = ~1.0 meq/L). The highest alum+acid dose (18 mg/L+20% H₂SO₄) was needed to remove more than 50% of the alkalinity in the system (Fig. 3).

It should be noted that equilibrium, especially with respect to pH, was reached only very slowly. For these experiments, small (approximately mL) quantities of alum solutions were added to relatively large volumes of lake water (e.g., 4 L) as would be done in field applications. The solutions were vigorously mixed on a stir plate with a 6 cm magnetic Teflon stir bar during alum addition and for about 20-30 min thereafter. Following that period, solutions were regularly stirred by hand prior to any sampling. Immediately after alum addition, the pH decreased from about 9 down to 6.8 – 8.2 depending upon percent acid in the formulation. pH then increased over the period of several days before asymptotically approaching an equilibrium value (Fig. 4).

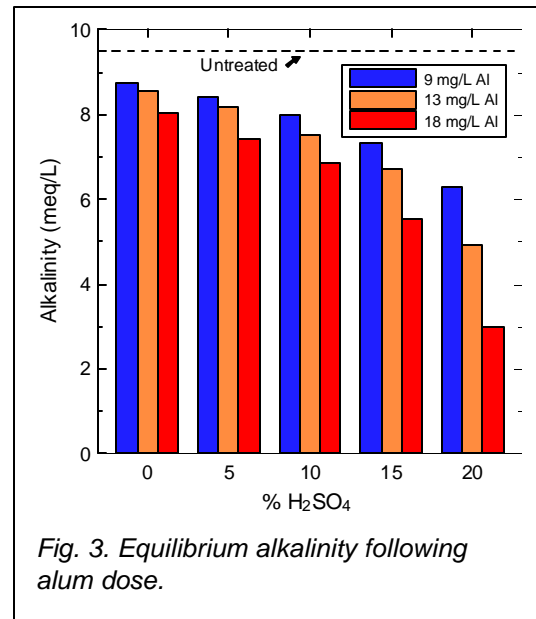
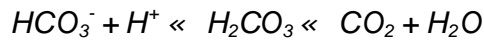


Fig. 3. Equilibrium alkalinity following alum dose.

The slow approach to equilibrium results from the conversion of HCO_3^- (and any CO_3^{2-} present, although only about 9% of the inorganic carbon is predicted to be in the carbonate form). The reaction of bicarbonate with protons can be written as:



That is, the bicarbonate ion (HCO_3^-) reacts with a proton (H^+) to form carbonic acid (H_2CO_3). Carbonic acid subsequently dissociates to form CO_2 (g) and H_2O . In the final step, the CO_2 (g) escapes to the

atmosphere. The protonation reaction is rapid, proceeding essentially at the diffusion-controlled limit. However, the formation of CO_2 and its volatilization out of water can be quite slow, and is apparently responsible for the slow increase toward an equilibrium pH value observed in Fig. 4.

This increase in pH over time was also found to affect dissolved Al concentrations (Fig.5). Dissolved concentrations increased over time, following the increased pH and resultant formation of $\text{Al}(\text{OH})_4^-$ and other Al species in solution (Fig. 5). Initial concentrations (at 1 h) decreased with increasing acid content of the particular alum treatment following well-known Al solubility relations; for example, the 9.2 mg Al/L dose at 0% H_2SO_4 , which bore the highest initial pH (8.2), also had the highest initial dissolved Al concentration (about 0.6 mg/L). In comparison, the highest acid treatment (20% H_2SO_4) had the lowest initial pH (about 7) and lowest dissolved Al concentration (0.02 mg/L) (Fig. 5). These concentrations then increased; the dissolved Al concentration for the 0% H_2SO_4 increased more than three-fold, from 0.5 to 1.6 mg/L, while the 20% H_2SO_4 increased from ~0.02 to 0.5 mg/L (Fig. 5).

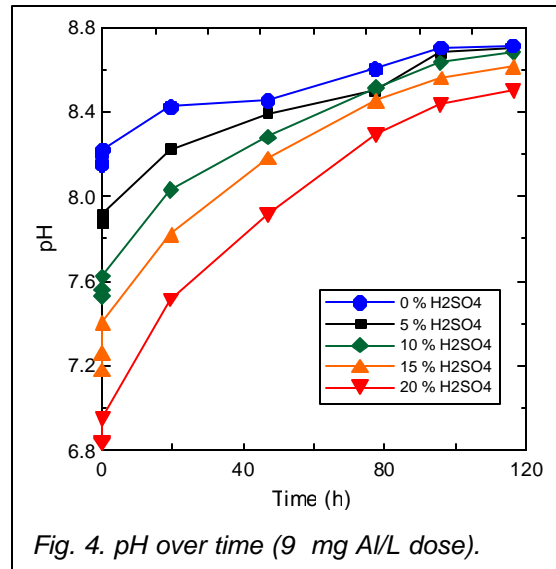


Fig. 4. pH over time (9 mg Al/L dose).

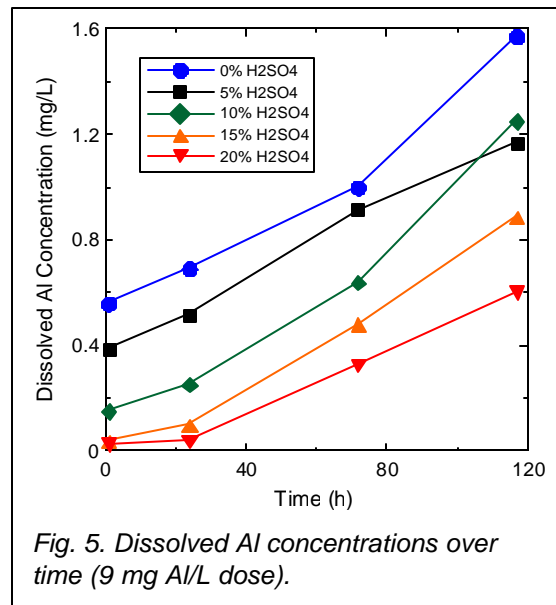
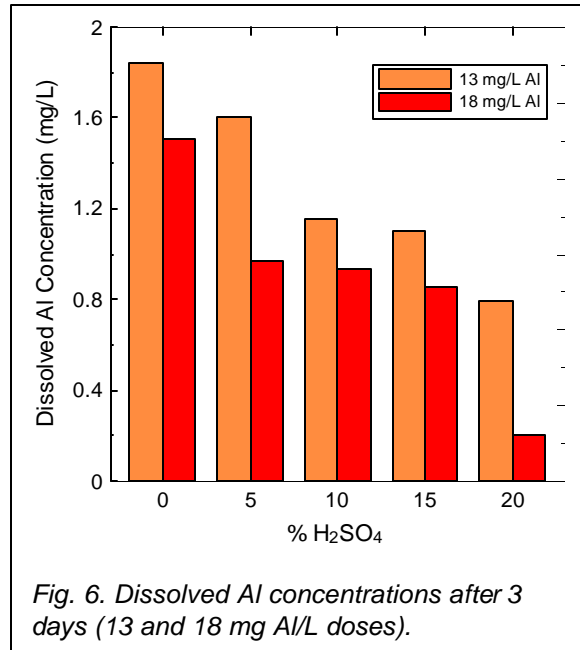


Fig. 5. Dissolved Al concentrations over time (9 mg Al/L dose).

Dissolved Al concentrations for lake water samples dosed to 13 and 18 mg/L Al with alum and high acid alum after doses were measured after 3 days (Fig. 6). It should be pointed out that a smaller volume of lake water were used for these determinations (0.5 L). As a result, a slightly different mixing and thus kinetic response from Figs. 4 and 5 would be expected, making direct comparison with the dissolved Al concentrations from the 9 mg/L equilibrations difficult. This point will be made clearer later in this section.

It is useful to compare the observed dissolved Al concentrations with theoretical concentrations based upon the chemistry of the lake water and common geochemical phases controlling Al solubility. To do this, theoretical Al concentrations were calculated using the USEPA geochemical equilibrium model MINTEQA2 (USEPA, 1991). Recent chemical analyses of Lake Elsinore water were used along with titration results from these samples as model input (Table 2).



Component	Units	Concentration
Ca ²⁺	mg/L	20.5
Mg ²⁺	mg/L	35
Na ⁺	mg/L	425
K ⁺	mg/L	29
Cl ⁻	mg/L	420
SO ₄ ²⁻	mg/L	450
Alkalinity	meq/L	9.6
pH	-	9.0

Sodium is the dominant cation in the water, while Cl⁻ and HCO₃⁻ (*i.e.*, alkalinity), along with SO₄²⁻, are the principal anions in the system. It is particularly relevant to note

the very low Ca:HCO₃ ratio (about 0.1 in concentration units of equivalents/L). Evaporation of water with a concentration ratio (in equivalents/L) less than 1 results in precipitation of CaCO₃ (s), lowering of the solution Ca levels, and an increase in the excess HCO₃⁻ concentration over time. (Drever, 1988). Continued evaporation will yield a high pH, high alkalinity water.

In contrast, evaporation of water with a Ca:HCO₃ ratio >1 yields in a low alkalinity, moderate pH water due to precipitation of CaCO₃, lowering of HCO₃⁻ and an increase in the excess Ca concentration over time. This chemistry is more common than that found in Lake Elsinore. For example, the water of the Colorado River has a Ca:HCO₃ ratio of about 2; as a result, even after extensive evapoconcentration, the pH and alkalinity in the Salton Sea (which is about 20x more saline than Lake Elsinore) remain quite moderate (pH 8.2 - 8.5, alkalinity ~ 4.3 meq/L). That is, the precipitation of CaCO₃ forms a “chemical divide” that, depending upon the chemical composition of the water, dictates the subsequent geochemistry of the water as it evaporates (Drever, 1988).

This geochemistry also directly influences Al solubility. For reference, two different Al phases commonly assumed to control Al solubility were used, a relatively soluble amorphous Al(OH)₃ solid phase and a crystalline Al(OH)₃ (gibbsite) phase (Lindsay and Walthall, 1989). The Al solubilities as a function of pH for these two phases are shown as solid lines in Fig. 7. Aluminum solubility increases with increasing pH from a dissolved concentration of about 0.16 mg/L at pH 7 to 4 mg/L at pH 8.8 for the amorphous Al(OH)₃ phase (Fig. 7). The crystalline gibbsite phase supports much lower dissolved Al concentrations (<0.01 - 0.1 mg/L). It is particularly interesting to note that the observed Al concentrations in the alum-treated waters fell below the predicted solubility for amorphous Al(OH)₃ but well above the gibbsite solubility line. It appears that some other Al phase with an

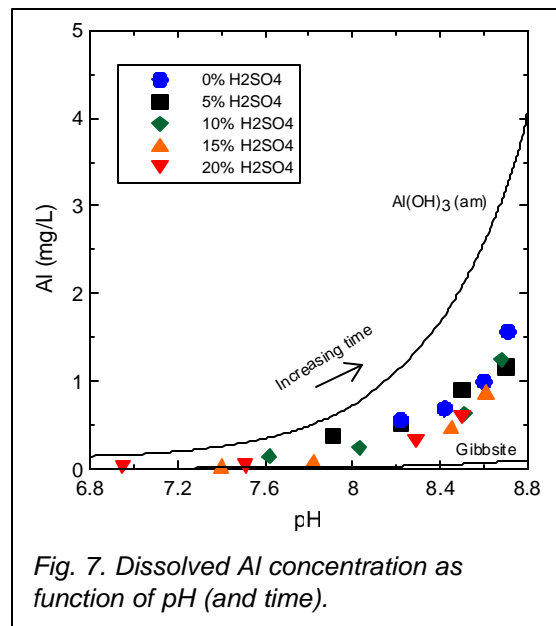


Fig. 7. Dissolved Al concentration as function of pH (and time).

intermediate solubility is forming upon hydrolysis and precipitation within the lake. The nature of this phase is presently under investigation. (It should be noted that speciation of the 0% H₂SO₄ solution, with its higher alkalinity and lower sulfate concentration,

yielded predicted Al concentrations that were within 0.3% of the levels predicted for the 20% H₂SO₄ solution, with its lower alkalinity and higher sulfate concentration.)

To evaluate the evolution of pH and dissolved Al concentrations in Lake Elsinore following alum addition, an additional study was conducted. Specifically, three identical 3 L samples of Lake Elsinore water were spiked to an Al concentration of about 9.2 mg/L (0% acid) under different mixing regimes: air-sparging, rapid mechanical mixing on a stir plate, and a slow mix (briefly mixed by hand each day following the initial rapid mixing during alum addition). pH values were measured at short intervals immediately after alum addition (Fig. 8a) and longer intervals over the next 8 days (Fig. 8b).

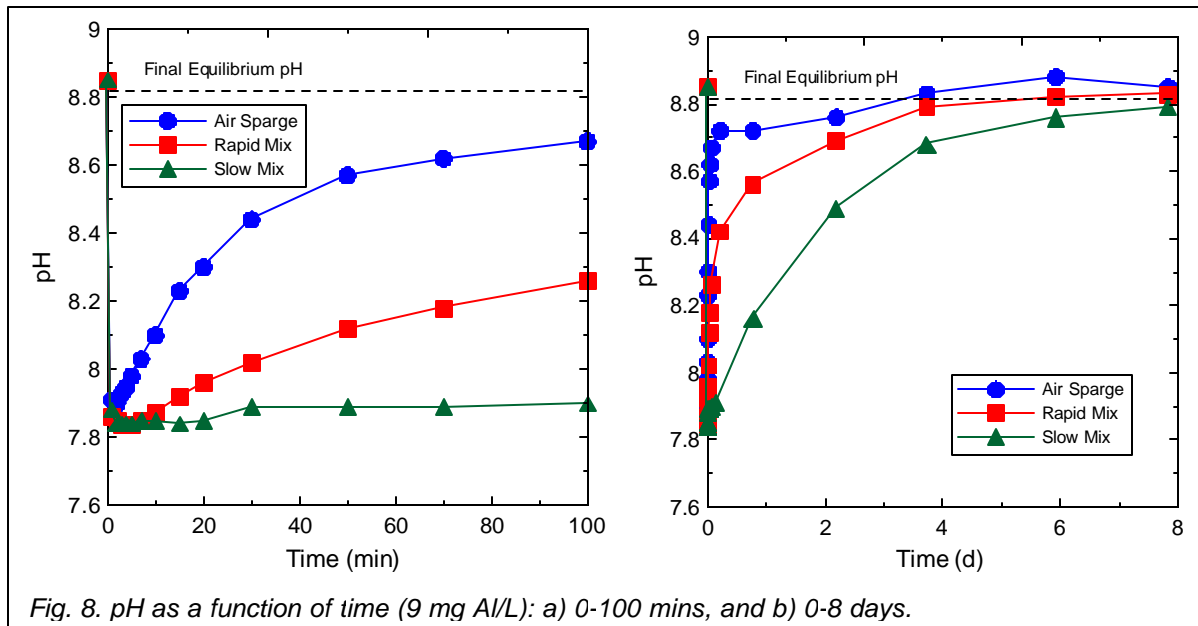


Fig. 8. pH as a function of time (9 mg Al/L): a) 0-100 mins, and b) 0-8 days.

The rate and nature of mixing had a profound effect on the rate of approach to an equilibrium pH value. Air-sparging, which would maximize the transfer of CO₂ (g) out of the water, resulted in a rapid increase in solution pH, exceeding a pH of 8.65 after 100 min (Fig. 8a). In comparison, rapid and slow-mixed solutions reached pH values of only about 8.3 and 7.9, respectively. In fact, only after 6 days did the slow-mixed solution approach the equilibrium pH value of about 8.8. It is difficult to design a laboratory mixing regime that adequately mimics that which would take place in the lake following alum application, however, it is clear that air-sparging would substantially overestimate the rate of CO₂ outgassing and pH equilibration in the field. It is proposed that the field conditions would probably lie in between the rapid and slow mix regimes; thus it seems reasonable to assume that 4 – 8 days will be required to approach an equilibrium pH value in Lake Elsinore following treatment.

Dissolved Al concentrations were also followed over this same time period for the 3 differentially-mixed systems (Fig. 9). Dissolved Al concentrations all started out around 0.2 mg/L immediately after alum addition (total Al concentrations were 9.24, 9.36 and 9.47 mg/L for air-sparged, rapid-mix and slow-mix systems, respectively). In the air-sparged system, the dissolved Al concentration rather closely followed the rapid rise in pH (Fig. 8b) and reached a steady-state concentration near 3 mg/L within a few hours (Fig. 9). The rapid-mixed system reached a dissolved Al concentration of about 2 mg/L after a few hours and then increased slowly over the next several days to reach the concentration present in the air-sparged system. The slow-mix system maintained dissolved Al concentrations lower than either the air-sparged or rapid-mix systems. As described previously, the lower dissolved Al concentrations imply formation of a less-soluble Al phase under these conditions.

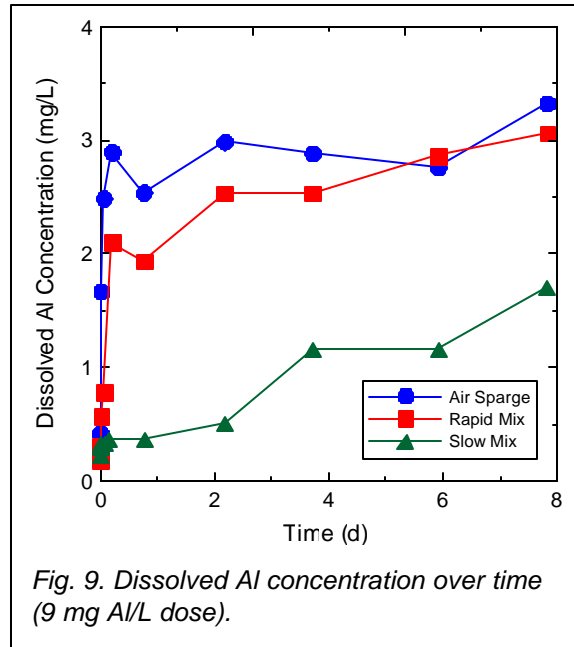


Fig. 9. Dissolved Al concentration over time (9 mg Al/L dose).

The dissolved Al concentrations for the air-sparged and rapid-mixed systems increased with increasing pH and approximately followed the Al concentrations predicted for a system in equilibrium with amorphous $\text{Al}(\text{OH})_3$ (Fig. 10). The slow-mixed system exhibited lower dissolved Al concentrations (similar to those shown in Fig. 7), again, suggestive of a phase intermediate in its crystallinity and solubility between amorphous $\text{Al}(\text{OH})_3$ and crystalline gibbsite. While the nature of this particular study did not allow an evaluation of the long-term solubility trends, crystallization kinetics would suggest that the dissolved Al concentrations would decrease over

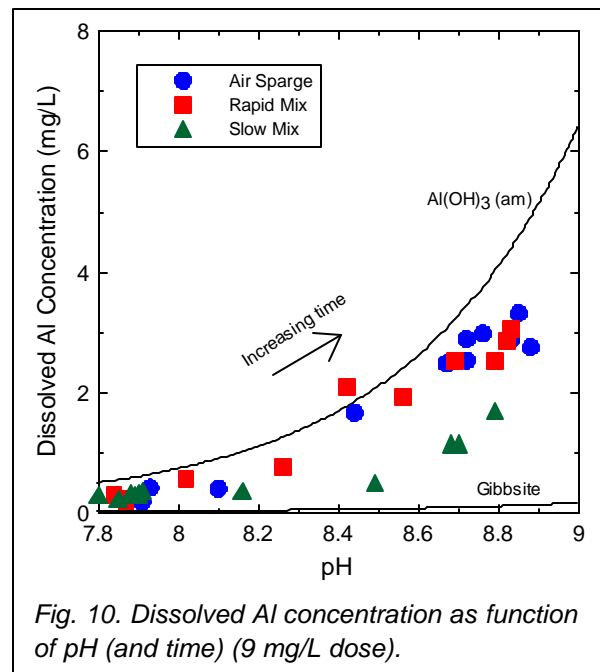


Fig. 10. Dissolved Al concentration as function of pH (and time) (9 mg/L dose).

time as the amorphous phase(s) transformed to lower solubility crystalline phases. This hypothesis is tested in longer-term experiments discussed below.

The improvements in water clarity that might be expected following alum additions under the different conditions described above (i.e., different Al doses and different percent free acid in the formulations) were also investigated. For this analysis, an *in vivo* fluorescence technique was used to measure chlorophyll concentrations in untreated and alum-treated samples several days after treatment. Measurements were made on a Perkin-Elmer LS-1000 fluorescence spectrophotometer at an excitation wavelength of 430 nm and an emission wavelength of 664 nm (APHA, 1989). A 1-cm pathlength quartz cell with about 2 mL of unfiltered samples was used in the analyses.

The 9.2 mg/L Al dose reduced chlorophyll concentrations about 16% relative to the untreated lake water, with no significant influence of acid content of the alum (Fig. 11). Higher doses were more effective, with some incremental benefit from increased acid content of the alum (Fig. 11). The relatively modest improvements in chlorophyll concentrations following alum addition no doubt result from the high equilibrium pH of the solutions. First of all, the high pH inhibits formation of the Al floc through maintenance of high

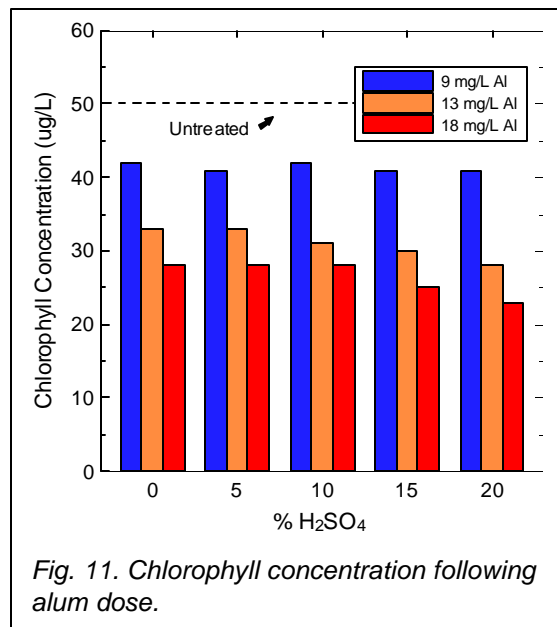


Fig. 11. Chlorophyll concentration following alum dose.

soluble Al concentrations (e.g., Figs. 6 and 9). Secondly, at high pH values, the surface of the Al(OH)₃ floc can approach neutral or even net negative charge, reducing its effectiveness at sorbing negatively charged cell surfaces and other particles in water. Higher Al doses and lower water column pH values would promote more dramatic improvements in water clarity.

Total dissolved solids (TDS) concentration in the lake water was not altered to any substantive degree by addition of alum or high acid alum. TDS was estimated from electrical conductance (EC) of the solutions and was in fact observed to decrease slightly with treatment. For example, in the 9.2 mg/L Al dose, TDS values decreased from 1.937 g/L for the untreated lake water, to 1.884 g/L for the regular alum, reached a minimum value of 1.881 g/L for the 5% acid alum, and then increased with increasing

acid content to 1.913 g/L for the 20% acid formulation. It appears that acidification removed sufficient alkalinity to actually lower slightly the EC and TDS in the samples. Removal of HCO_3^- (formula weight of 61 g/equivalent) from solution as CO_2 and replacement with an equivalent of SO_4^{2-} (formula weight of 48 g/equivalent) should, in principle, yield a slight decrease in TDS.

In light of geochemical considerations, an experiment was conducted to quantify the influence of Ca^{2+} addition on pH and alkalinity in Lake Elsinore water. As noted above, the low Ca: HCO_3^- ratio of the lake water promotes the high pH, high alkalinity conditions found in Lake Elsinore following extended drought conditions (e.g., at the end of the drought in 1992, the pH in Lake Elsinore had increased to greater than 9.5). Such high pH conditions would favor desorption of PO_4 from added $\text{Al}(\text{OH})_3$ and any native $\text{Fe}(\text{OH})_3$ due to dissociation of H^+ from surface hydroxyl groups and reversal of surface charge from a net positive charge to a net negative charge. (Note that the zero-point-of-charge for these minerals is at pH approximately 8 - 8.8.)

Calcium chloride was added to 0.5 L of Lake Elsinore to bring the final Ca^{2+} concentration from 20 mg/L in untreated samples to 40, 80, 140, 260 and 420 mg/L. The precipitation of CaCO_3 is generally written as:



where the precipitation reaction removes 2 equivalents of alkalinity per mole of Ca^{2+} . As one can see from the above equation, CO_2 is produced during CaCO_3 precipitation as well as during the acid neutralization reactions described previously. Thus, a decrease in pH was noted following addition of Ca^{2+} to lake water, especially at large doses where

the high degree of supersaturation would hasten the rate of crystal formation, followed by a gradual increase in pH (not shown). The pH increase was attributed to outgassing of CO_2 , until approximate equilibrium was attained between all phases (Fig. 12). Thus, addition of Ca^{2+} and precipitation of excess alkalinity is an alternative way to lower the pH, although addition of almost 200 mg/L (or 8×10^6 kg Ca^{2+}) would be needed to shift the system

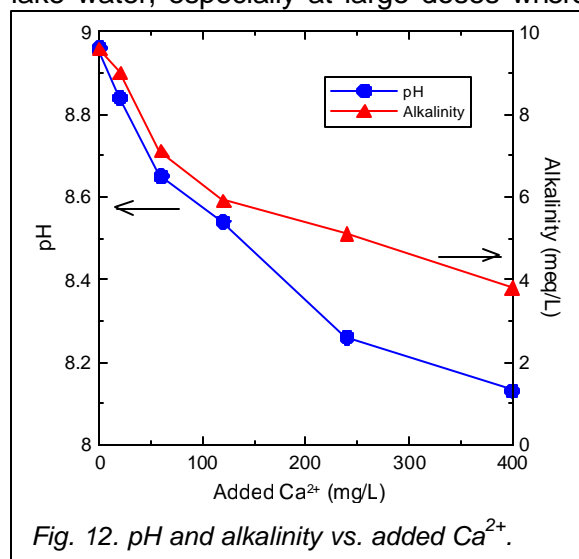


Fig. 12. pH and alkalinity vs. added Ca^{2+} .

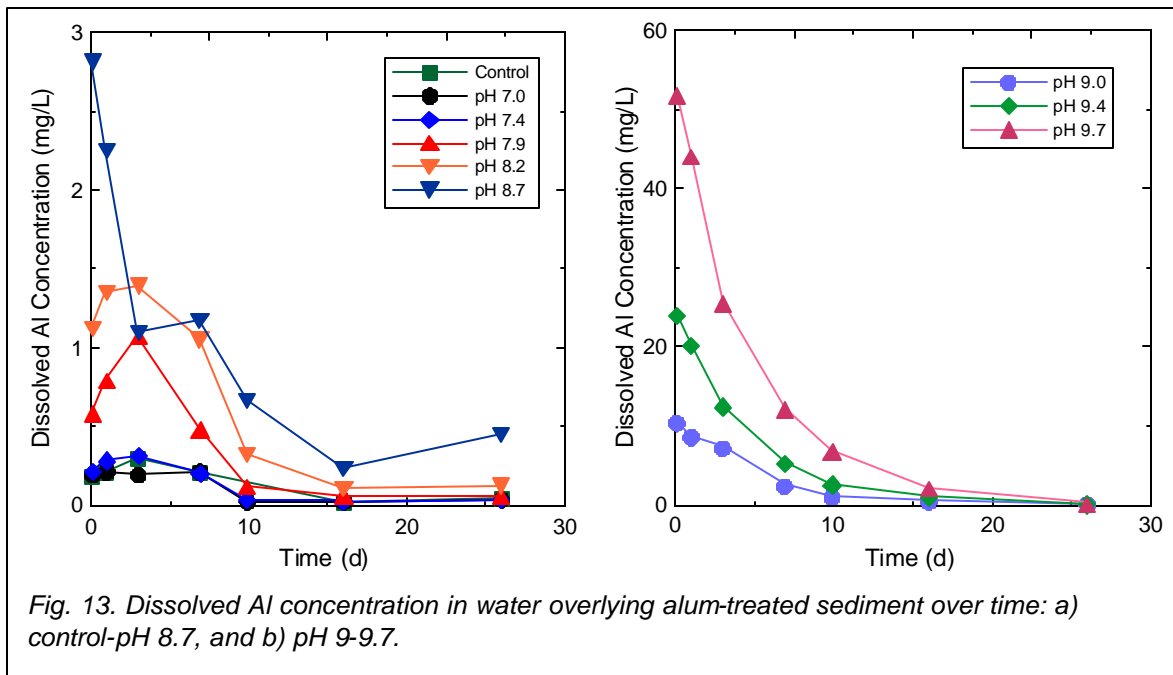
back to the favorable side of the chemical divide (i.e., excess Ca^{2+}) that would promote

moderate pH values and low alkalinity. It is suggested that a calcium treatment be applied in conjunction with an alum treatment to (i) help drive down the pH of the system and (ii) establish a more favorable Ca:HCO₃ ratio.

3. Resolubilization Potential of Alum Floc

In addition to the changes in water column chemistry following alum addition, a core study was conducted to evaluate the potential for resolubilization of the aluminum floc with an increase in pH of the overlying water. A series of intact cores, similar to those used for nutrient flux measurements, were collected on 19 October 2001 from near the center of the lake (in fine organic, type-III sediments). Alum was then added to the overlying water to bring a final Al dose equivalent to 48 g/m². The alum was partially neutralized with NaOH prior to addition to the cores to help minimize acidification of the overlying water. Nine cores were maintained at pH values that ranged from 7.0 and 9.7 by simultaneous addition of H₂SO₄ or NaOH with the alum. Separately, 2 cores were initially brought to pH ~7.5, maintained at this pH for approximately 48 h, and then raised to pH ~8.8 and 9.2. The pH of the overlying waters were generally measured every 1-3 days and adjusted with H₂SO₄ or NaOH as needed for the next. Samples were collected every 1 – 3 days during the initial study period and 5 - 10 days later in the study.

Dissolved Al concentrations followed pH-solubility relationships (*i.e.*, increased concentration with increased pH), and also generally decreased quite substantially over time (Fig. 13). Approximately 2 h after alum addition, dissolved Al concentrations ranged



from ~0.2 mg/L at pH 7 (Fig. 13a) to >50 mg/L at pH 9.7 (Fig. 13b). The Al concentrations in the high pH samples (pH 8.7 - 9.7) decreased over time, while concentrations in the lower pH samples (7 - 8.2) actually increased slightly over the first 3 days before dropping to concentrations <0.5 mg/L.

The concentration of Al in the two cores that were allowed to equilibrate at pH 7.5 for about 2 days before being raised to pH 8.8 or 9.2 remained relatively low; in fact, the higher pH equilibration maintained lower dissolved concentrations than that at a slightly lower pH, where more variability was witnessed (Fig. 14). Nevertheless, dissolved Al concentrations remained well below those in equilibrium with an amorphous $\text{Al}(\text{OH})_3$ phase (calculated 4 - 8 mg/L).

This data was also plotted as a function of pH to explicitly show the relationship between observed and theoretical Al solubilities (Fig. 15). This is relevant because the pH of the samples did tend to drift somewhat over time, requiring regular readjustment. As a result, the pH at the time of sampling (prior to any subsequent pH adjustment) did vary. The key feature to consider from Fig. 15 is that the Al concentrations for samples taken later in the experiment (e.g., 10-26 days), were much lower than those found early in the study (e.g., 0.1 - 3 days). That is, dissolved Al concentrations roughly followed the theoretical solubilities for an amorphous

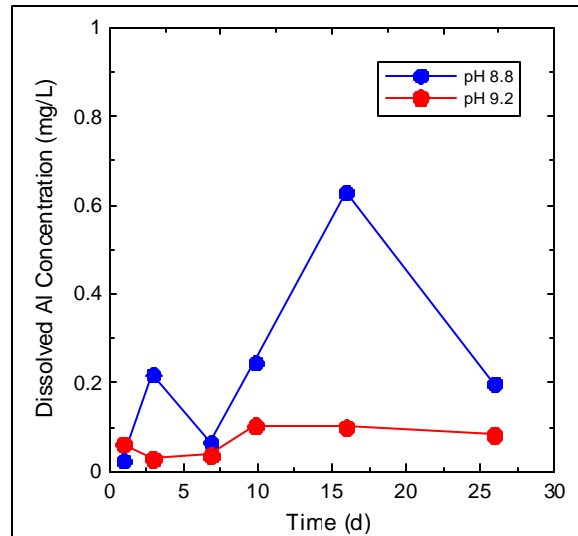


Fig. 14. Dissolved Al concentration in water overlying alum-treated cores over time. Cores adjusted to pH 7.5 for ~2 days, then adjusted to pH ~8.8 and 9.2.

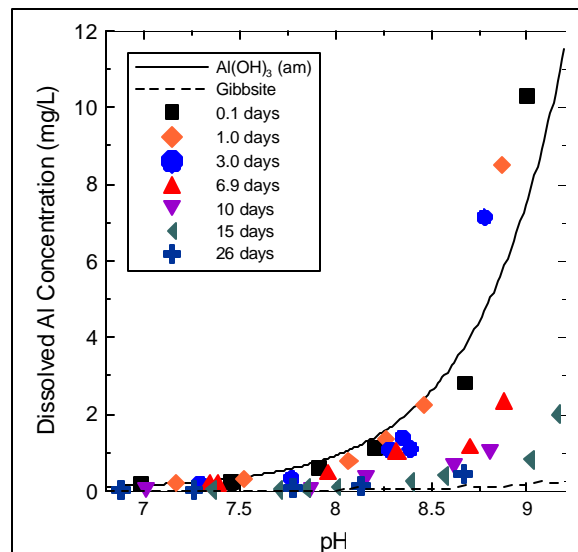


Fig. 15. Dissolved Al concentration in water overlying alum-treated cores as function of pH and time.

Al(OH)₃ phase early (0.1 – 3 days); upon aging, the Al floc apparently transformed to a more crystalline phase which bore a lower Al solubility although the dissolved concentrations remained above those predicted for gibbsite.

Conclusions

The high pH and alkalinity of Lake Elsinore present unique challenges to effective chemical control of SRP flux. Relatively high Al solubilities can be expected following alum or high-acid alum additions. A particularly interesting result from these studies was the slow approach to an equilibrium pH value following Al addition. The pH decreased sharply upon treatment, and then increased at a rate dependent upon the rate of mixing. Aeration promoted a rapid increase in pH that, in turn, resulted in a rapid increase in dissolved Al concentrations. On the other hand, very slow mixing, without aeration, maintained a low pH for several days due to the slow rate of CO₂ outgassing; dissolved Al concentrations increased slowly over this time period, and maintained lower levels at equivalent pH values when compared with the aerated sample. A rapidly mixed, unaerated sample was intermediate in its rate of pH and Al change over time. Nevertheless, all 3 mixing regimes yielded equivalent final pH and alkalinity levels. The results indicate that mixing plays an important role in defining the dissolved Al concentrations present in the lake following treatment. Longer-term (~1 month) studies using alum-treated cores revealed a general decrease in dissolved Al concentrations over time, presumably reflecting the transformation of highly soluble, amorphous Al phases to low solubility, crystalline phases.

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