

Quarterly Report
for
Reducing Eutrophic Conditions of the
Salton Sea

(The Second of Four)

Prepared for the
State Water Resources Control Board

Date: 4/1/04
Contractor Name: The Salton Sea Authority
Funding Program: State Prop 13
Contract #: 02-051-257-1

Principal Investigators:
Prof. Chris Amrhein, Assoc. Prof. Michael Anderson, and Prof. Mark Matsumoto,
University of California Riverside

CONTENTS

Table of Figures	3
Table of Tables.....	4
Table of Photos	4
Introduction.....	5
Project Tasks	6
Task 5. Modifying existing P removal systems (52% complete)	6
Task 6. Conduct laboratory-scale studies of P-removal (66% complete).....	10
Task 7. Conduct meso-scale tank studies of P-removal (0% complete).....	23
Task 8. Conduct ditch-scale studies for P-removal (50% complete).....	24
Task 9. Conduct CEP treatment trials (0% complete)	31
Task 10. Monitor biological Se-uptake and evaluate CEP for Se-removal (43% complete) 32	
Task 11. Determine the effects of turbidity in a CEP (0% complete)	34
Task 12. Prepare cost projections (0% complete).....	35
Task 13. Quarterly, Draft and Final Reports (20% complete).....	35
References	36

Distribution List

University of California, Riverside: Chris Amrhein, Chris Goodson, Brooke Mason
Kent SeaTech: Jack VanOlst
State Water Resources Control Board: Nadim Zeywar
Salton Sea Authority: Dan Cain

Table of Figures

Figure 1. Measured turbidity after 10 minutes settling time in vial tests with changing ferric chloride and polymer concentrations for the Celanese cationic guar polymers a)T-4141 and b) CP-14.	13
Figure 2. P _T concentrations observed from alum and cationic polymer CP1160 additions after 10 minutes settling time in a 25 mL vial test.	15
Figure 3. P _S concentrations at different settling times with 4 ppm Al additions in Whitewater River trials of Jar Tests.	18
Figure 4. P _T concentrations at different settling times with 4 ppm Al additions in Whitewater River trials of Jar Tests.	19
Figure 5. Relationship between total phosphorus and turbidity in Whitewater River jar tests. ..	19
Figure 6. P _T removals with varying alum additions in Whitewater River jar tests.....	20
Figure 7. Turbidity removal in CEP water in the dark with alum.	22
Figure 8. Total phosphorus removal in CEP water in the dark with alum.....	22
Figure 9. Measured EC affect of a 300 g sodium sulfate slug 188 ft. from the input on 2/5/04.	26
Figure 10. Total phosphorus concentrations in response to varying alum-Al additions on 1/22/04.	28
Figure 11. Dissolve reactive phosphorus concentrations in response to varying alum-Al additions on 2/5/04.....	29
Figure 12. Decreases in percent initial turbidity with increasing alum additions on 2/5/04.	30
Figure 13. Raw water aluminum concentrations on 2/5/04.	30

Table of Tables

Table 1. Modified project work schedule with cumulative percentages of tasks completed.	6
Table 2. Compilation of Lab-Scale Tests performed as of 3/1/04.....	11
Table 3. P _T removal in Whitewater River Jar tests using alum, no polymers.	20
Table 4. Baseline conditions for alum ditch trials with Whitewater River water.....	25
Table 5. River and CEP water sampling sites.....	32
Table 6. Fall/Winter '03/'04 conditions in the Salton Sea's tributary rivers.....	34

Table of Photos

Photo 1. The coagulation, flocculation, sedimentation (CFS) unit.....	7
Photo 2. The simulation drainage ditch. a) The weir-boarded monk box and potential mixing tanks for flocculant treatments. b) A view of the outflow monk box.	8
Photo 3. The drained CEP algal harvest section with sedimentation belt.	9
Photo 4. The drained CEP algal harvest section with sedimentation belt.Photo 4.	10
Photo 5. Phipps & Bird 2L jar tester apparatus with CEP water during initial mixing stage.....	17
Photo 6. Injection tubes dripping the alum solution into the inflow monk box on 2/24/04.	27
Photo 7. Floc formation at a) 25 ft. and b) 175 ft. with 7 mg Al/L and 55 gpm of WWR water.29	
Photo 8. Model scale CEP.	35

Introduction

The Salton Sea is California's largest inland water body and home to more species of birds than any other place in California. Over 390 species of birds, including the endangered brown pelican and Yuma clapper rail, have been identified at the Sonny Bono Salton Sea National Wildlife Refuge. Eutrophication of the Salton Sea has sufficiently impacted its beneficial uses (including recreation, fishing, and wildlife resources) that TMDLs for pollutants causing this impairment may soon be implemented. Some of the specific effects of eutrophication include high algal biomass, high fish productivity, low clarity, frequent very low dissolved oxygen concentrations, massive fish kills, and noxious odors. External loading of nutrients, particularly phosphorus (P), is responsible for the eutrophication of the Salton Sea. Because internal phosphorus loading in the Salton Sea is low and external phosphorus loading to the Sea is high, reduction of tributary phosphorus loading to the Salton Sea may reduce eutrophication.

The first goal of the project is to determine the efficacy of removing phosphorus from water that eventually discharges into the Salton Sea. Because the Salton Sea is phosphorus limited, removing phosphorus and sediment from agricultural drainage water (ADW) should reduce the overall amount of phosphorus entering the Sea via local rivers and thereby decrease eutrophication. Although phosphorus and suspended solids removal is commonly practiced in municipal wastewater treatment, the high sediment concentrations and salinity of the ADW will require testing and possible modification to the typical procedures used in municipal wastewater treatment.

All of the tributaries to the Salton Sea contain low concentrations of selenium. There is some concern about the potential for selenium bioaccumulation at the various stages of treatment. With this in mind, our second project goal is to monitor selenium levels at each stage of the CEP and flocculation treatment processes. Currently, most scientists believe that selenium is sequestered in the Salton Sea due to the high salinity and is not likely to cause the types of serious environmental impacts that have occurred at Kesterson Reservoir and other sensitive sites. However, if future plans to reduce salinity in the Sea are enacted, there may be a need to consider treating the tributaries for selenium in addition to phosphorus. During these studies, we will monitor selenium at each step of the process and note any bioaccumulation that may occur. If these monitoring efforts indicate that a potential problem exists, we will seek additional support from outside agencies to investigate techniques for selenium control. There have been several promising studies that indicate that managed high-rate algal ponds, very similar to those used in the CEP process, may be able to concentrate low levels of selenium and allow them to be removed in a cost-effective manner.

Project Tasks

The cumulative percent completion to date for each task and its subtasks is noted next to each task's title herein. Also, Table 1 is a modified project work schedule that summarizes this information.

Table 1. Modified project work schedule with cumulative percentages of tasks completed.

Project Task	Year/Quarter/Month																	
	2003			2004										2005				
	4th			1st			2nd			3rd			4th			1st		
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M
5. Modifying existing pilot-scale P-removal systems	24%			24%														
6. Conduct laboratory-scale studies of P-removal	33%			33%														
7. Conduct bench-scale CFS studies of P-removal																		
8. Conduct ditch-scale studies for P-removal				50%														
9. Conduct CEP flocculant/ polymer treatment evaluations																		
10. Monitor biological Se-uptake and evaluate CEP for Se-removal	21%			21%														
11. Determine effects of turbidity on a CEP																		
12. Prepare cost projections																		
13. Quarterly, draft and final reports	10%			10%														

Task 5. Modifying existing P removal systems (52% complete)

5.1 Bench-scale unit

A bench-scale coagulation, flocculation, sedimentation (CFS) unit will be used to evaluate the behavior of chemical flocculants and polymers in a simulated full-scale conventional water treatment system (see Photo 1).

Photo 1. The coagulation, flocculation, sedimentation (CFS) unit.



Located in Mark Matsumoto's laboratory at UCR, the CFS system consists of an integrated chemical mixing chamber, three-stage flocculator, and inclined-plate sedimentation tank apparatus. The system allows one to monitor the effects of a specific water treatment over a 10 hour period. In the past, treatments were performed on 300 gallon water samples trucked in from the CEP and Salton Sea tributaries in 50 gallon drums.

The drawback with this approach is that only one treatment can be tested on one 300 gallon sample at a time and it is a challenge to keep the sample water's solids in suspension. We are also lacking a reproducible method for assessing numerous treatments on all three river waters: the Alamo, New, and Whitewater Rivers. Accordingly, we are now considering the possibility of installing the CFS in a mobile laboratory trailer owned by the Salton Sea Authority. This would allow us to perform extended trials on agricultural wastewaters taken directly from their sources. First, we need to continue to determine the best chemical treatments for Whitewater River water in jar test, simulation drainage ditch, and CEP trials (Tasks 6, 8, and 9). Lastly, we can compare how those same treatments would work on all three river waters in the CFS, a flow-through system that would allow us to make highly controlled comparisons of chemical treatments on-site. Therefore, we propose to postpone the use of the CFS until later on in the study.

5.2 Simulated drainage ditches

Three 100 gallon tanks were installed at the input end of the simulation agriculture drainage ditch to mix the chemical amendments before ditch application (Photo 2). A 1/20 hp variable speed motor was ordered for the mixing tanks to prepare the solution at the site. Peristaltic pumps with multiple flow heads were installed to provide the various application rates of the chemical mixtures to the inflow monk box.

The water inflow valve for the ditch was moved to the inflow monk box for ease of operation. Additionally, a second control valve was installed in preparation for the second ditch that will be installed during summer, 2004.

A V-notch weir was installed that can manage flow rates up to 120 gallons/min. An attached ruler was used to measure flow rates once calibrated against the filling time for a 5 gallon bucket. Sample points were flagged every 25 feet along the ditch. Flow rates used during the alum ditch trials were between 50 and 100 gallons per minute. By running at these higher flow rates, we were able to decrease the ditch's retention time to <30 minutes.

Photo 2. The simulation drainage ditch. a) The weir-boarded monk box and potential mixing tanks for flocculant treatments. b) A view of the outflow monk box.



5.3 Optimization of Selenium Uptake by Algae in the CEP

Although the CEP was designed for phosphorus removal, selenium could also be removed by bioaccumulation and “bioflocculation” of the captive algae and fish populations, and

thus improve the effluent water quality. Starting in July 2004, we will make modifications of the water velocity and the circulation rate through the algal settling zone in the CEP to optimize selenium removal.

This quarter, the algal harvest section of the CEP was drained to make modifications to the sedimentation belt (Photo 3). Transverse cleats were attached to the belt with special ribbed elevator bolts to prevent the cleats from loosening. In addition, two of the three belt guide rollers were repositioned to reduce wear on the belt cleats. The belt itself also was realigned on the drum, to promote smooth operation. The CEP system is now ready for the chemical flocculation trials that will be initiated next quarter. Alum, ferric chloride, and several polymers will be tested for their ability to assist in harvesting algae during the cool season.

Photo 3. The drained CEP algal harvest section with sedimentation belt.



A total of 2,000 to 2,500 pounds of tilapia are needed to prepare the CEP cages for the next set of experimental trials. To date, 1,600 pounds of tilapia have been harvested and moved to holding cages supplied with warm water (Photo 4).

Photo 4. The drained CEP algal harvest section with sedimentation belt. Photo 4.



In addition, several operational improvements for the CEP process are being discussed with our colleagues at Clemson University. These include modifications of the water flow through the fish holding sections as well as changes in water depth.

Task 6. Conduct laboratory-scale studies of P-removal (66% complete)

Introduction

In Dr. Chris Amrhein's laboratory at UC Riverside, we are screening chemical coagulants and polymers for their capacities to reduce turbidity and remove total and soluble phosphorus (P_T and P_S , respectively). These laboratory tests are being performed on samples of river water from the Coachella and Imperial Valleys (The Whitewater, New, and Alamo Rivers), and Algae Zone water from the Controlled Eutrophication Process (CEP) at Kent SeaTech. Testing is being done in both 25 mL glass vials and 2 L jars.

Bulk water samples are collected from the Whitewater River and CEP Algae Zone, transported back to UC Riverside, and refrigerated until analysis (see Table 2 for sample dates). In the lab, different concentrations of both coagulant and polymer are tested on the sample water to establish their capacities for phosphorus removal.

Table 2. Compilation of Lab-Scale Tests performed as of 3/1/04.

Sample Water	Coagulant Aid	Polymer Type	Polymer Company	Mixing Method	Date Collected
*CEP	FeCl ₃	T-4141	Celanese	Vial Test	10/27/2003
	FeCl ₃	CP-14			
	Alum	T-4141			
	Alum	CP-14			
	Alum	2J			
	Alum	21J			
	Alum	T-4246			
	Alum	AP1100	GE Betz	Jar Test	2/3/2004
	Alum	AP1120			
	Alum	AP1142			
	Alum	CP1155			
	Alum	CP1160			
		Alum, Light, 10°C			
		Alum, Dark, 10°C			
		Alum, Light, 22°C			
	Alum, Dark, 22°C				
**WWR	Alum		GE Betz	Jar Test	1/7/2004
	Alum	AP1100			

*CEP: Controlled Eutrophication Process

**WWR: Whitewater River

Vial Tests

Method and Materials

During vial tests, polymer and a coagulant, either alum or ferric chloride, were gravimetrically added to 25 mL clear glass vials. The vials were then filled to 25 mL with test water and placed on an Eberbach Corp. shaker (Ann Arbor, MI) on low for 3 minutes. After 10 minutes settling time, the turbidity was measured, and a 7 mL sample was pipetted from the top 1/3 of the vials and analyzed for P_S and P_T.

Turbidity was measured in the 25 mL vials with an HF Scientific, Inc. Micro 100 Turbidimeter (Fort Myers, FL). Then, both dissolved reactive phosphorus (P_S) and total phosphorus (P_T) concentrations were analyzed on aliquots using methods described in Standard Methods for the Examination of Water and Wastewater (1992). Sample preparation for P_S analysis included filtration (< 0.45µm, Fisherbrand Membrane) and acidification with 1 drop of concentrated sulfuric acid, which decreased the pH to approximately 2.5. The samples

were then analyzed with a modified ascorbic acid-molybdate blue method on an Astoria-Pacific Int. Alpkem RFA 300 Autoanalyzer (Clackamas, OR).

For P_T determination, 5 mL of acidified, unfiltered sample and 1 mL of oxidation solution were combined in 10 mL mailing tubes and digested using the persulfate digestion method found in Standard Methods with the following modifications: The oxidizing solution was made of 30 g boric acid, 350 mL 1 N NaOH, and 50 g $K_2S_2O_8$ diluted to 1 L with deionized water. Samples were heated in a boiling water bath for 1.5 to 2 hours then analyzed for P_T using the Alpkem RFA 300 Autoanalyzer.

The initial vial tests focused on the coagulant ferric chloride ($FeCl_3$) and polymers T-4141, CP-14, T-4246, 2J, 21J (Celanese Corporation, Jeffersontown, KY). These polymers included two polyacrylamide (PAM) polymers and three polysaccharide (guar) polymers. The anionic PAMs included 21J and 2J, with 21J possessing a higher charge density. The cationic guar polymers are T-4141 and CP-14, with T-4141 having the highest charge density, and one anionic guar was used, T-4246 (Malik and Letey 1991). None of the Celanese trials included a cationic PAM.

In later lab scale studies, the choice of coagulant changed from ferric chloride to alum, $Al_2(SO_4)_3 \cdot nH_2O$ $n=12-14$, Technical Grade Fisher Scientific) since alum is the most widely used coagulant in wastewater treatment plants to reduce the turbidity and phosphorus concentration (Hammer and Hammer 1996). The alum concentration was determined based on the aluminum (Al) content.

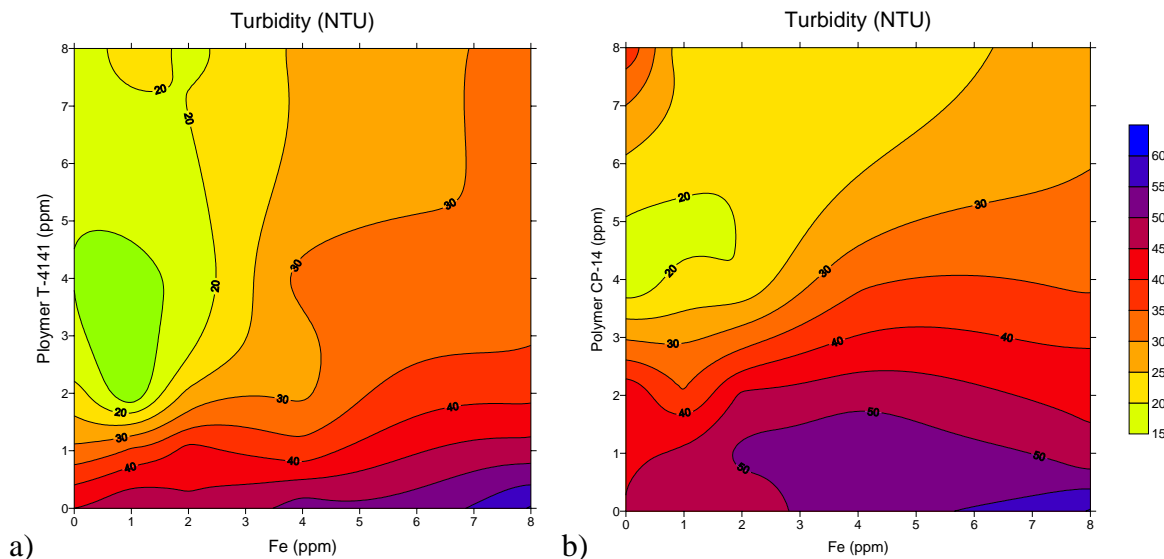
Results and Discussion

Vial tests served as a laboratory screening tool to provide a quick determination of coagulant and polymer flocculation capabilities. In the initial vial tests, conducted with CEP water, we measured both P_S and turbidity, but not P_T . However, we found a strong linear correlation between turbidity and P_T ($r^2=0.82$) in later CEP water tests, which suggests that turbidity can be used to estimate P_T concentration. The following discussion of ferric chloride and polymer vial tests is based on this correlation.

Celanese polymers were added to CEP water in varying concentrations to determine the combined effect of the coagulant, ferric chloride, and the coagulant aid, polymer. Both cationic guar polymers showed similar effects in the reduction of turbidity. Higher polymer additions with lower ferric chloride concentrations gave the largest reduction in turbidity (Figure 1). The reductions in turbidity were highest at polymer and ferric chloride concentrations of 1 and 2 ppm (76% removal), respectively for T-4141 and 0 and 4 ppm for CP-14 (65% removal). These removals

were induced by the increase in polymer concentration, not iron concentration. Vial tests with iron (III) chloride did not include the anionic polymers, so no comparison can be made between anionic or cationic polymer effects for the reduction of turbidity.

Figure 1. Measured turbidity after 10 minutes settling time in vial tests with changing ferric chloride and polymer concentrations for the Celanese cationic guar polymers a) T-4141 and b) CP-14.



When alum was combined with the cationic polymers, T-4141, and CP-14 the vial tests showed good removal between initial and final turbidity readings after 10 minutes of settling. As seen before in the ferric chloride tests, the reduction in turbidity was more a function of the increase in polymer concentration than an increase in alum concentration. The highest turbidity removals, 65% and 53%, were obtained using T-4141 (2 ppm polymer and 0 ppm Al), and CP-14 (8 ppm polymer and 2 ppm Al), respectively.

The anionic polymers did not significantly reduce the turbidity (data not shown). The highest turbidity removals for the anionic polymers were only 19.6, 18.3, and 7.5 % for T-4246, 2 J and 21J, respectively. These results suggest that the capacity for a polymer to remove turbidity is dependent on its charge type and charge density. For example, the highest cationic charge density polymer (T-4141) had the best removals while the highest anionic charge density polymer (21J) gave the poorest turbidity removals.

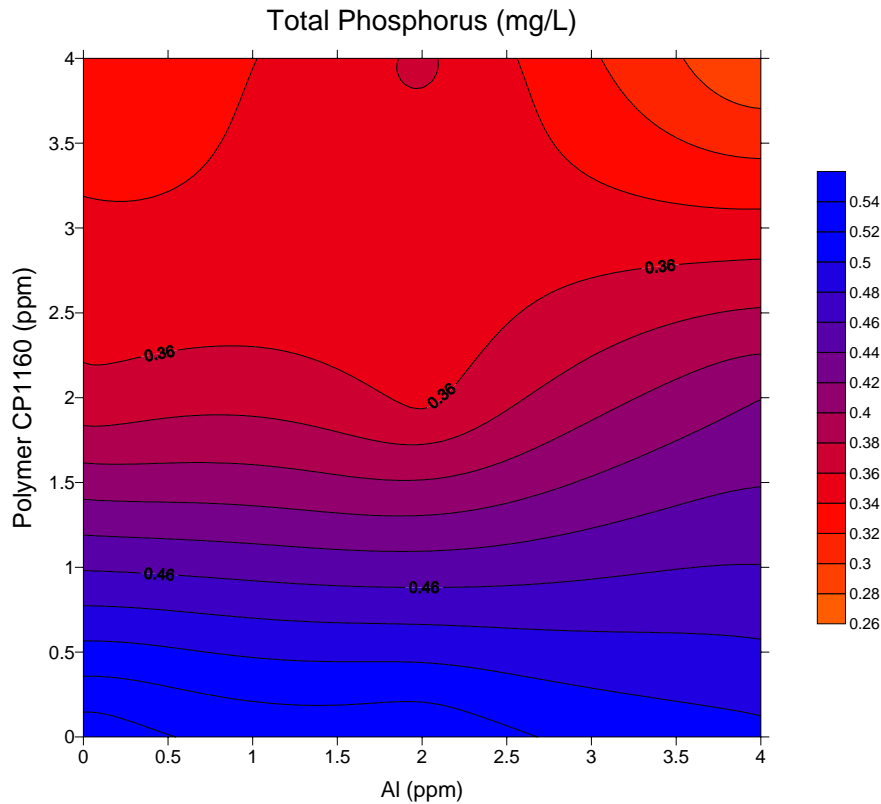
The Celanese Corporation, manufacturers of the previously tested polymers, could not be located. Therefore, we concluded that the Celanese Corporation can not serve as a reliable source for future polymer purchases. Another company, GE-Betz, provided eleven powdered PAM polymer samples for the study. These powder polymers will be easier to transport and use

at the field sites compared to the emulsions explored in the preliminary tests. These GE-Betz polyacrylamide polymers range in charge type, molecular weight, and charge densities.

A subset of the GE-Betz polymers was chosen for the lab screening tests. This subset includes AP1100 and AP1120 (both anionic), AP1142 (nonionic), and CP1155 and CP1160 (cationic). These polymers were chosen to represent the wide range of molecular weights and charge densities available in the given set of 11 polymers. From this point forward the study will focus around GE-Betz polymers with hopes that GE-Betz will be able to reliably and consistently supply high-quality products.

As with the Celanese polymers, only the cationic GE-Betz polymers showed reductions in turbidity and P_T concentration when combined with alum. Polymer CP1160 showed the best removals at 4 ppm Al and 4 ppm polymer additions, which reduced the turbidity by 49% and the P_T concentration by 68% (Figure 2). The other cationic polymer tested, CP1155, had similar results at the same Al and polymer concentrations, reducing turbidity by 42%, and P_T by 61%. CP1160 has a lower cationic charge density than CP1155, which contradicts the observation of the Celanese polymer tests, where the higher the cationic charge density polymer showed higher P_T removals. Further analysis in the jar tests could explore the ideal cationic charge density of a polymer for the maximum P_T removals. Although the highest removals occurred at the highest tested concentration of polymer and alum (4 ppm of each amendment), like the Celanese cationic PAMs, the phosphorus and turbidity removals were more influenced by the concentration of polymer than the concentration of alum (Figure 2). Both the Celanese and GE-Betz polymers were consistent with each other, demonstrating significant reduction in algae water turbidity with the addition of a cationic polymer.

Figure 2. PT concentrations observed from alum and cationic polymer CP1160 additions after 10 minutes settling time in a 25 mL vial test.



In these 25 mL vial tests, only cationic polymers reduced turbidity in CEP water. These removals were influenced mostly by the increase in polymer additions, not increases in alum additions. Previous studies of algae flocculation have noticed similar results in polymer and algae interactions. McGarry (1976) conducted a lab experiment using jar tests, algae water, and 27 polymer additions with varying concentrations of alum. In this study of cationic, anionic and nonionic polymers, only the cationic polymers were effective in reducing algal turbidity. The most significant floc formation occurred at 15 mg/L alum addition, and 6 mg/L of a cationic C31 polymer. However, McGarry noted that the cationic polymer did not flocculate without the addition of alum. The degree to which alum aids flocculation can be better investigated in 2L jar tests.

Conclusion

The vial tests were a fast method to determine relative activities of the polymer and coagulant in the test solutions. These tests were included in the report because they were initially used as the first stage in determining which polymers work the best for phosphorus removals.

However, from this point forward, jar tests will take precedence as the lab scale test of choice. The small sample size and reduced volume of the vial tests did not allow for a realistic comparison to field-scale tests, like the ditch-scale investigations. When floc formed in the vial tests, it fell to the bottom of the vial and accumulated. This settled matter, either algae or sediment, obstructed the light transmission during the turbidity measurement. Also, the 25 mL vial reduced the amount of mixing that could occur. When the vial was filled to a 25 mL volume, the headspace was reduced, so that when the vial was capped and shaken, there wasn't a large enough air bubble to ensure mixing. As a result, floc formation was not induced to the degree that it was in jar tests. We concluded that this vial test procedure is far inferior to the larger scale jar tests.

Jar Tests

Method and Materials

Jar tests were used to improve upon the methodological problems of the vial tests. The jar tests used 2 L square beakers on the Phipps & Bird PB-700 6 paddle jar tester apparatus (Richmond, VA) (Photo 5). The jars were filled with river water or CEP water to the 2 L mark, and an initial sample was collected from either the top of the jar, or the tube, which is located 10 cm below the top level of water. Then, desired volumes of stock solution of either the coagulant alum and/or flocculant (GE-Betz Polymer) were added to the jars.

Photo 5. Phipps & Bird 2L jar tester apparatus with CEP water during initial mixing stage.



The mixing procedure included a rapid mix at 300 rpm for 1 minute, then a moderate mix at 80 rpm for 30 minutes. The jars were then removed from the apparatus and allowed to settle undisturbed for a measured amount of time. Sampling from the top was employed for the majority of the measurements. These samples were taken from the top quarter of the height of the jar, approximately 4 cm below the surface of the water. Twenty-five mL were collected using a Rainin pipette. The tube 10 cm below the surface of the water was the sample port in some jar tests when parameters like light, bubbles, or temperature were tested in the promotion of algae flotation. The analysis of turbidity, P_S , and P_T followed the methods described in the vial test section.

Results and Discussion

Alum Trial

Water from the Whitewater River was initially used in the jar tests to support the field trails, which were being started at Kent SeaTech. However, polymers with different charge types, charge densities, and molecular weights will be investigated in future jar tests so that ideal combinations of alum and polymer can be determined for field-scale application.

The initial jar tests measured the effectiveness of the alum treatment alone. The dissolved reactive phosphorus dropped by approximately 70% within 1 minute of settling and

remained at this level (Figure 3). This immediate reduction indicates that alum adsorbs dissolved reactive phosphorus almost instantaneously. The total phosphorus data show that alum alone is capable of removing more than 80% of the total phosphorus after 20 minutes of settling time (Figure 4). We observed that the turbidity was correlated with the total phosphorus concentration. The linear relationship between the turbidity and P_T in jar test sub samples taken at regular intervals had an average r^2 value of 0.9985 (Figure 5). This relationship is expected since phosphorus binds strongly to suspended solids, specifically organic matter and clay particles. The total phosphorus concentration was dependent on the amount of suspended solids in the river. It follows that if amendments like alum and polymer are successful in reducing the turbidity, then the total phosphorus concentration will be reduced as well. The settling times required for adequate removal of phosphorus and turbidity are anticipated to decrease with the addition of polymers.

Figure 3. P_S concentrations at different settling times with 4 ppm Al additions in Whitewater River trials of Jar Tests.

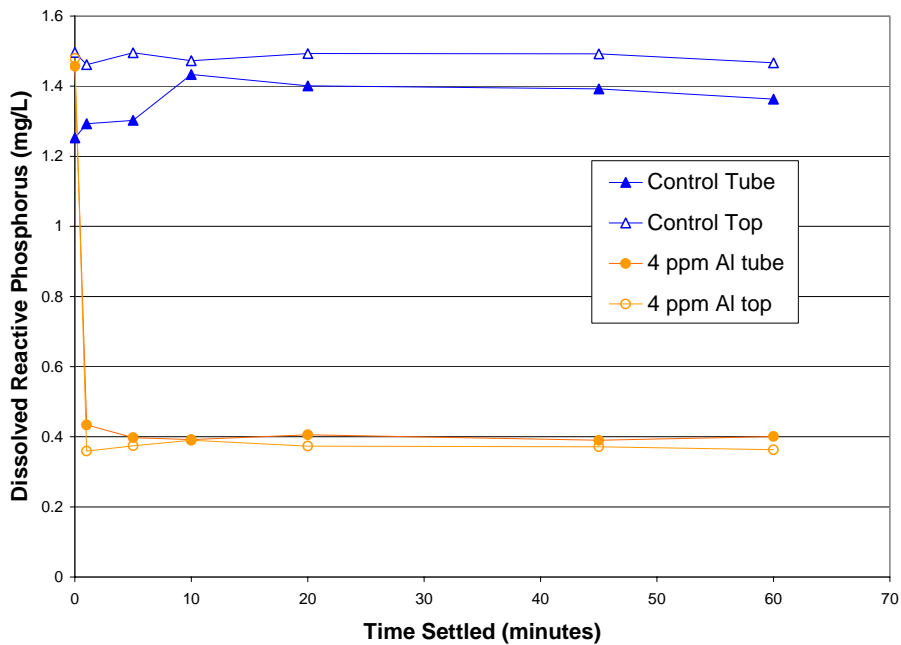


Figure 4. P_T concentrations at different settling times with 4 ppm Al additions in Whitewater River trials of Jar Tests.

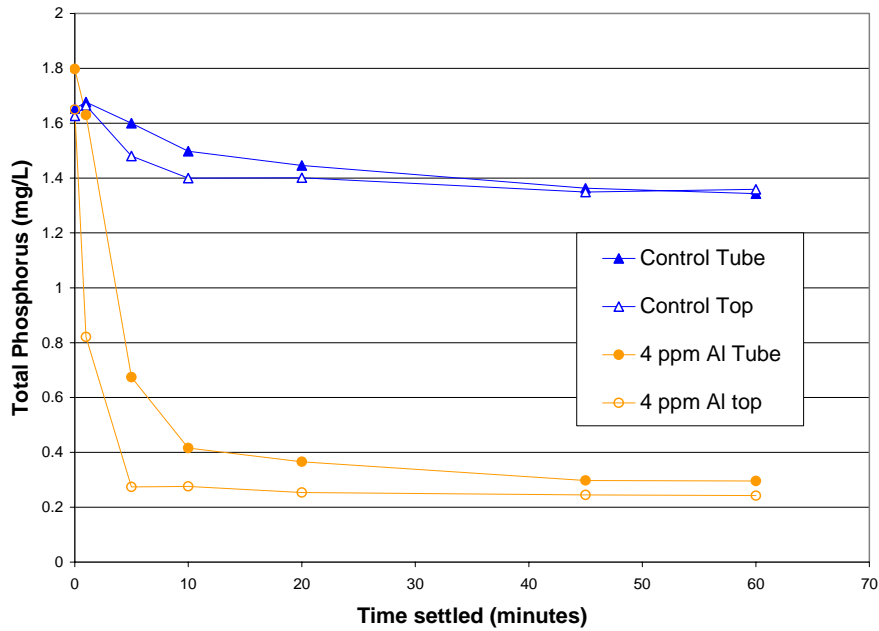
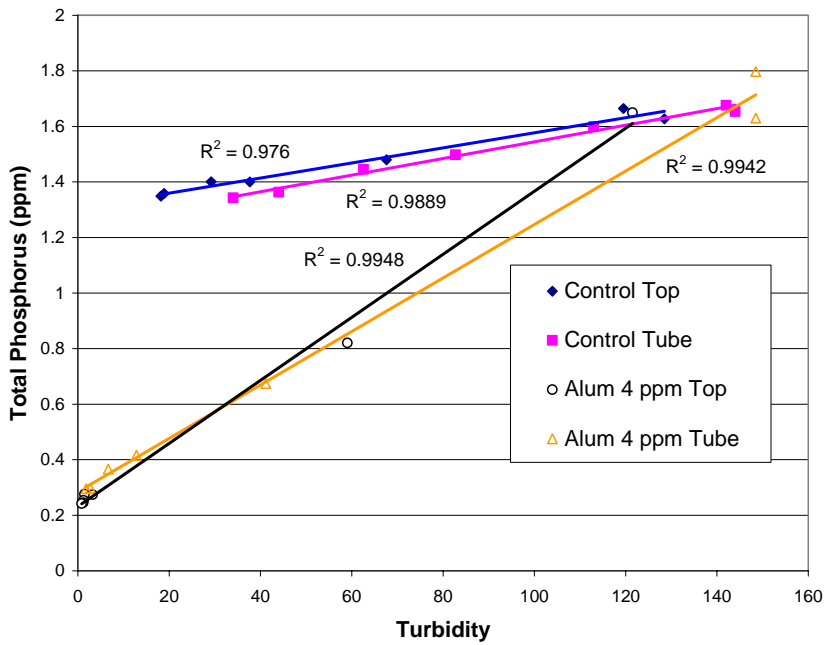


Figure 5. Relationship between total phosphorus and turbidity in Whitewater River jar tests.



The initial jar tests with Whitewater River water showed that as the alum concentration increased, P_T decreased (Figure 6). There was a large difference in phosphorus removals from 0 to 2 ppm Al added, yet phosphorus removal did not change as much when the concentration was doubled from 4 to 8 ppm Al (Table 3). After 10 minutes of settling, the majority of P_T removal had taken place. Beyond 10 minutes of settling time, the change in phosphorus removal was negligible.

Figure 6. P_T removals with varying alum additions in Whitewater River jar tests.

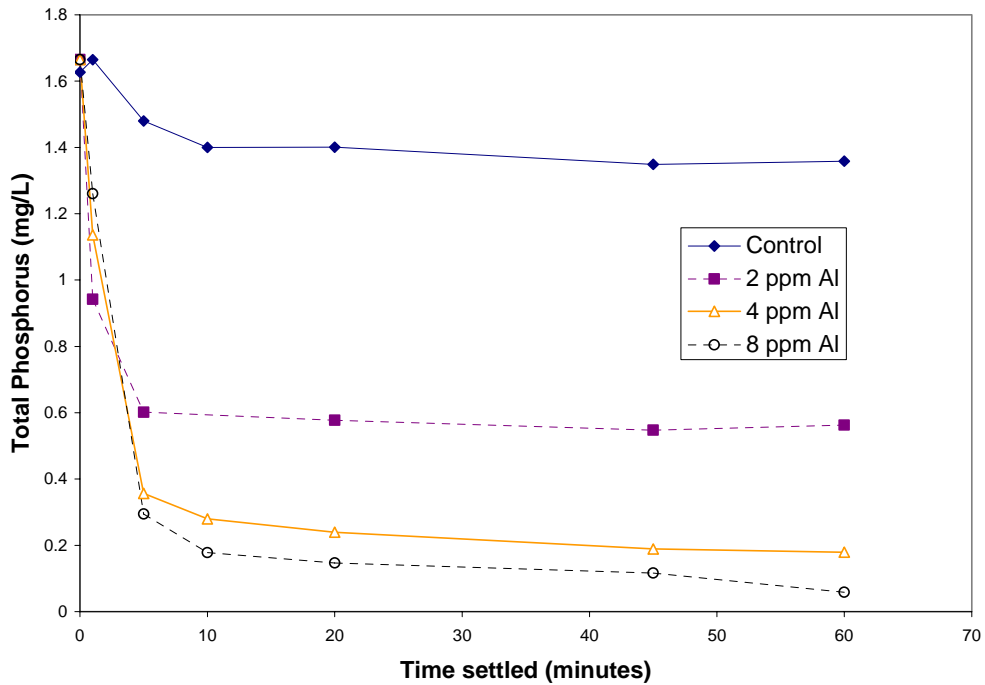


Table 3. P_T removal in Whitewater River Jar tests using alum, no polymers.

Time settled (minutes)	Percent removal of total phosphorus Al ppm additions			
	0	2	4	8
1	-2.3	43.3	31.8	24.3
5	9.04	63.8	78.6	82.3
10	14	N/A	83.2	89.3

While running the jar tests on the CEP water, we notice that some of the algae-floc would float rather than settle. We hypothesized that the flocculation and flotation of algae is affected by the temperature, light, and bubble formation in the water sample. In light and warmer temperatures, one would expect a higher rate of algae production and photosynthesis. Photosynthesis releases O_2 to the water, which will form small bubbles attached to the algae or trapped in the algae-floc. The extra buoyancy provided by the oxygen causes the floc to float.

The effect of temperature on algae flocculation was studied at high alum concentrations and a wide range of temperatures in Al-Layla, 1973. In the study, increased temperatures actually hindered the capability of the alum to remove algae. Flotation of algae in this study occurred at temperatures warmer than 20°C and alum doses as high as 100 mg/L. In our CEP jar tests, water temperatures of 7.5°C and 22°C were tested and Al concentrations up to 8 ppm. Under these conditions, there was no effect of temperature on the efficiency of settling.

In both light and dark jar tests, the addition of alum showed an increase of turbidity after 1 minute of contact time (Figure 7). This indicates that while floc was successfully formed, little settling occurred during the initial contact between the alum floc and the algae. We observed higher floc formation rates with the 8 ppm alum addition. As settling time increased, a large accumulation of floc that had formed at the surface settled to the bottom of the jar. Overall, as the alum concentration and settling time increased, the turbidity and P_T decreased (Figure 8). We saw no evidence of increased flotation due to light, which might be attributed to the short time of observation (25 minutes). Air bubbled into the jars using a porous air-stone only circulated the algae-floc, which kept the turbidity relatively constant throughout the settling time period. Dissolved air floatation systems may be tested later using larger volumes and with smaller bubbles that will better attach to and float the floc to the surface.

Figure 7. Turbidity removal in CEP water in the dark with alum.

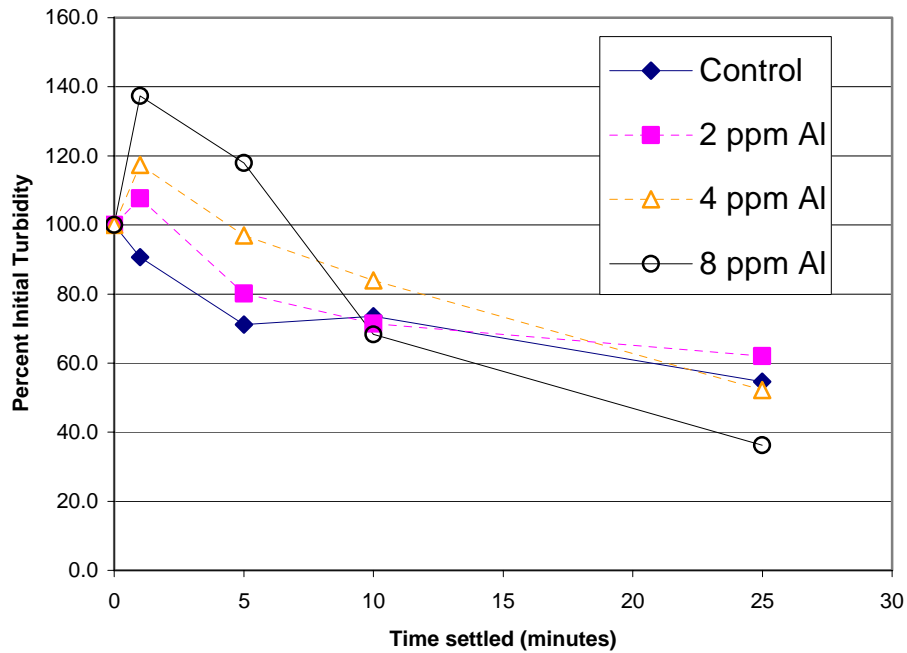
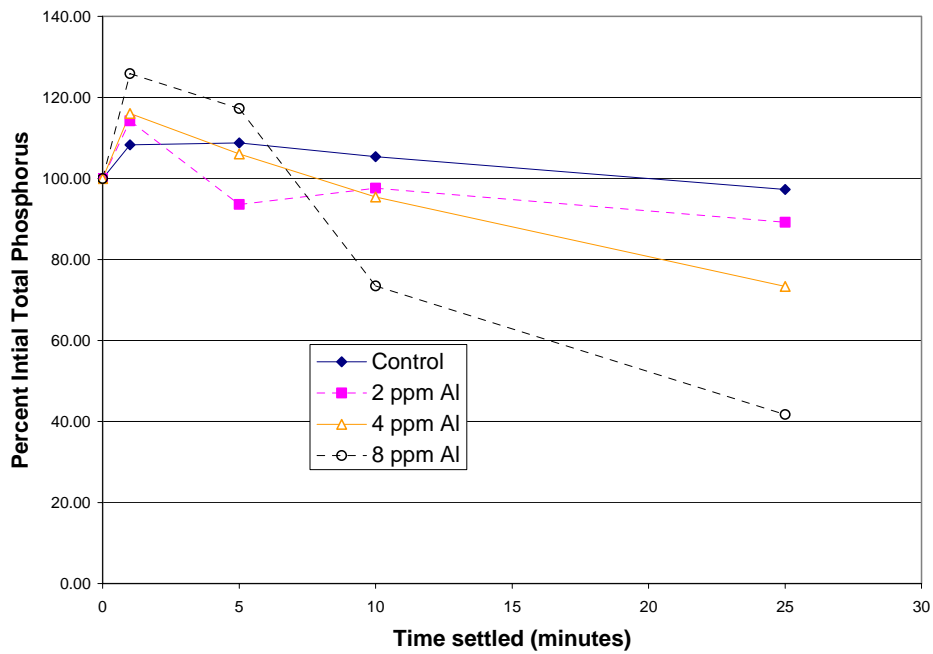


Figure 8. Total phosphorus removal in CEP water in the dark with alum.



Polymer Trials

Jar tests with both alum and 5 polymers (AP1100, AP1120, AP1142, CP1155, and CP1160) were tested with a 60 minutes settling time. This settling time was far too long to show any advantages of the polymer addition for a reduction in both turbidity and phosphorus. That is, after one hour settling, the alum-alone treatments and the alum plus polymer treatments had settled equally. Studies are underway to determine the kinetic effects of alum plus polymers additions on settling rate.

Conclusion

The addition of alum alone was successful for P_T removal in both Whitewater River and CEP water jar tests. Changes in experimental conditions, like temperature, light, and bubble additions, did not enhance the algae flotation in the CEP water jar tests. Other polymers will be investigated to determine an ideal coagulant aid for Whitewater River and CEP waters.

Preliminary Conclusions

These lab scale tests are the first step in identifying potentially effective chemical amendments for decreasing P_T in the rivers that feed into the Salton Sea. From here on, jar tests will serve as the sole laboratory scale test method for polymer evaluation since they are effective and widely accepted in the water treatment industry.

Alum treatments alone remove P_T in both Whitewater River water and CEP water effectively. In both the literature and our lab scale tests, cationic polymers enhanced P_T removals in CEP water. However, the apparent advantages of cationic polymers must be considered alongside their potential toxicity to aquatic organisms if used carelessly.

Polymer additions to the Whitewater River water did not increase the amount of P_T removal after one hour settling. Ongoing tests are determining the efficiency of P removal in the alum plus polymer system by sampling the suspensions after 1, 5, 10, 20, 45, 60 minutes.

Task 7. Conduct meso-scale tank studies of P-removal (0% complete)

As mentioned in Subtask 5.1, we intend to use the bench-scale CFS unit only after we've determined which treatments work best on Whitewater River water in Tasks 6, 8, and 9. Based on the results of these lab- and field-scale studies, CFS trials of phosphorus removal and sediment flocculation will be conducted starting in May, 2004. Agricultural drainage water will be pumped directly from the Whitewater, New and Alamo Rivers into the CFS, subjected to

chemical flocculation treatments, sampled, and discharged back into the river downstream. The UC Riverside staff will oversee the testing operation and apparatus, record background data, and collect water samples (pre-, during, and post-treatment) during treatment runs. The water samples will then be analyzed in Dr. Amrhein's laboratory at UC Riverside.

Task 8. Conduct ditch-scale studies for P-removal (50% complete)

This task involves pilot-scale evaluations of the Whitewater River implementing the best possible sediment and phosphorus removal techniques determined by the laboratory-scale studies described in Tasks 6. The 188 ft. simulated earthen agricultural drainage ditch described in Subtask 5.2 is being used for these trials.

8.1 Flocculant/polymer work plan for in-ditch treatment

Our current objectives are to implement amendment trials in the ditch that verify and expand upon our findings from lab-scale jar tests (Task 6). Though these results indicate that combinations of alum and anionic polymer did not decrease P_T concentrations, we hope that by adding anionic polymers to the ditch, perhaps downstream of the alum input, we may more successfully settle out alum floc. While equal parts alum and cationic PAM gave extremely effective removals in jar tests, the latter does present an ecotoxic risk.

Therefore, we intend to conduct alum and PAM ditch trials which will examine changes in P_T , P_S , and Turbidity in constant ditch flow rates by 1) adding 1- 10 ppm Al alone, 2) adding combinations of 1-5 ppm Al and 1-10 ppm anionic PAM, and 3) adding combinations of 1-5 ppm Al and 1-10 ppm cationic PAM. Sampling will occur at 25 foot intervals along the length of the ditch. The resulting P_T , P_S , and Turbidity data will be converted to percentages of the initial values (0 ft., 0 amendments) and plotted over the distance of the ditch. From these plots we can determine the equilibrium percent P_T , P_S , and Turbidity values for the given treatment. With this information, we can scale-up the treatments appropriately for the Alamo and New Rivers when we move on to performing CFS Trials (Task 7). It should also be noted that we will make attempts to measure residual amendment concentrations (namely Al and polymer) in water samples to attempt mass balance calculations and to evaluate the potential amendment loss from the ditch (specifically, cationic polymer).

8.2 Conduct in-ditch treatment trials

Introduction

Four alum ditch trials were conducted this quarter in the simulation drainage ditch at Kent SeaTech's Coachella Valley facility. These trials allowed us to screen alum for its capacity to remove P_T , P_S , and Turbidity from Whitewater River water along the 188 ft. length of the ditch.

Methods

For each day-long trial, we attempted to pump a constant flow rate of Whitewater River (WR) water into the ditch and monitor baseline conditions in grab samples (Table 4). Constant flow rates were achieved in all but the first trial. In this case, flow was decreased from 86 gpm (initial) to 78 gpm (final) due to partial blockage of the river water intake structure with flotsam part way through the day. It should be noted that on this day, upstream dredging of the river channel released large amounts of flotsam and caused some variability in our measurements (data not shown). However, these kinds of shifts in background conditions were accounted for in the calculations of percent initial P_T , P_S , and Turbidity that are discussed below.

Table 4. Baseline conditions for alum ditch trials with Whitewater River water.

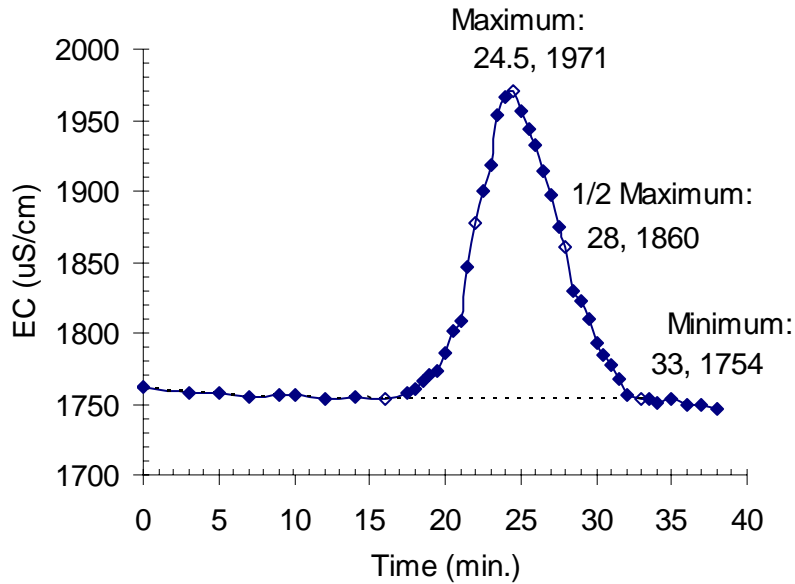
Trial	Date	Ditch Flow Rate (gal/min)	Turbidity (NTU)	EC (μ S/cm)	Water Temp. (deg. C)	pH	Total Phosphorus (mgP/L)	Dissolved Reactive Phosphorus (mgP/L)	Raw Water Al Conc (mgAl/L)
First	01/22/04	82	44	2104	-	7.0	1.8	0.5	2.0
Second	02/05/04	87	92	1953	18.0	-	2.0	1.1	2.8
Third	02/21/04	53	64	2015	17.9	-	1.5	1.2	1.6
Fourth	02/24/04	53	53	1997	17.6	-	1.3	1.1	1.6

- indicates data not recorded

We conducted tracer studies prior to the initiation of the first and second alum ditch trials to check the hydraulic characteristics of the ditch. Once a stable ditch flow rate was established, a slug of highly saline water was poured into the ditch inflow and a stopwatch started. We timed its elution through the ditch by observing electrical conductivity (EC) measured directly in the outflow drain with a portable EC probe (Fisher). From this data, we plotted Figure 9, for example. Here, we observed a residence time of 28.8 minutes, assuming that one half of the maximum EC equals the residence time. This figure agrees well with our geometric calculation of residence time, 27.3 minutes, based on measurements of ditch water surface area and depth (6.63"x36.75"x188') divided by flow rate (87 gpm). The fact that the salt peak eluted in a

uniform, bell-shaped curve with very little tapering and returned to the baseline EC values once past indicates that there are no hydraulic “dead zones” in the ditch.

Figure 9. Measured EC affect of a 300 g sodium sulfate slug 188 ft. from the input on 2/5/04.



After waiting two detention times, a series of baseline samples were taken along the length of the ditch. Then, injection of the first treatment directly into the inflow monk box was initiated. Stock alum solutions, 145 g/L of well water, were continuously mixed using a motorized impeller. Two peristaltic pumps with heads fitted with multiple tubes delivered the alum solution from the stock solution tank to the inflow monk box. There, the solution was dripped into the turbulent inflow, cascaded over the V-notched weir, and into the ditch (Photo 6). Alum injection rates were adjusted by adding or subtracting tubes connected to the peristaltic pump and calibrated using a graduated cylinder and a stop watch.

Photo 6. Injection tubes dripping the alum solution into the inflow monk box on 2/24/04.



Sampling for each treatment was done only after two residence times had elapsed from the treatment's initiation. Transects of grab samples were collected every 25 feet, 1 inch below the water surface, from the outflow to the inflow end in order to avoid picking up sediments stirred up by the pole sampler. For the "zero distance, zero treatment" sample that culminated each transect, the alum injection lines were set aside and the inflow monk box allowed to purge for two minutes before sampling directly from the monk box.

For each sample, three bottles were filled: One 25 mL glass scintillation vial was filled for turbidity, EC, and pH measurements. Two 60 mL Nalgene bottles were filled; the one for PS analysis was filtered into another 60 mL bottle then acidified, the one for P_T and Al analysis was just acidified. Acidification consisted of decreasing the samples' pH to approximately 2.6 by adding 1 drop of sulfuric acid. Samples were transported and stored in the dark and at 4° C. Raw water aluminum analysis was performed using a Plasma Quad ICPOES (Perkin Elmer, Wellesley, MA). See Task 6 for turbidity and Phosphorus analytical methods.

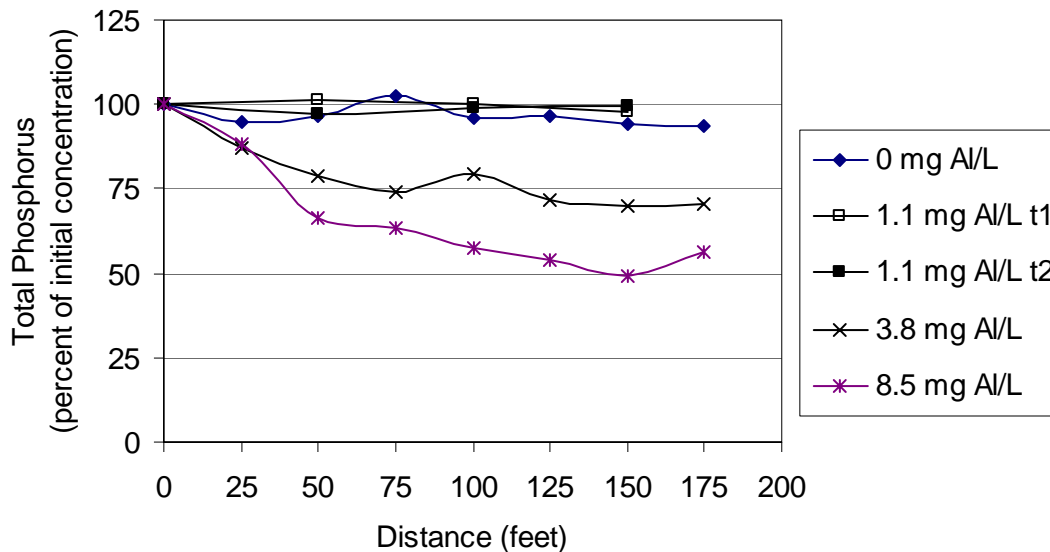
Results and Discussion

Total phosphorus removals in the first alum ditch trial were representative of the results from the other trials (Figure 10). In this trial, it was obvious that increasing alum-Al additions

cause decreases in total phosphorus. To date, our highest treatments of 9 ppm alum-Al alone decreased P_T to less than 50%.

However, we have yet to test still stronger treatments to see how much alum is required to decrease P_T down to nil. We did not anticipate needing to exceed 8 ppm alum-Al since the best jar tests performed in Task 6 decreased P_T to almost 10%. This may indicate that there are mixing power discrepancies between jar tests and ditch trials. To allow for better comparisons between all procedures, we are currently attempting to calculate G values (mean velocity gradients) for the systems used in each task.

Figure 10. Total phosphorus concentrations in response to varying alum-Al additions on 1/22/04.



As seen in Figure D, Alum capably decreased P_S concentrations to nil with 5.7 ppm Al. These observations agree well with the jar tests performed in Task 6. Considering the small changes in P_T concentrations relative to these P_S concentrations, it is possible that alum converts P_S into P_T to form light, settling-resistant floc. This theory is supported by observations of progressively thicker floating floc rafts down the length of the ditch that formed during higher alum (7 and 9 ppm Al), lower flow (53 gpm) treatment trials (Photo 7).

Photo 7. Floc formation at a) 25 ft. and b) 175 ft. with 7 mg Al/L and 55 gpm of WWR water.

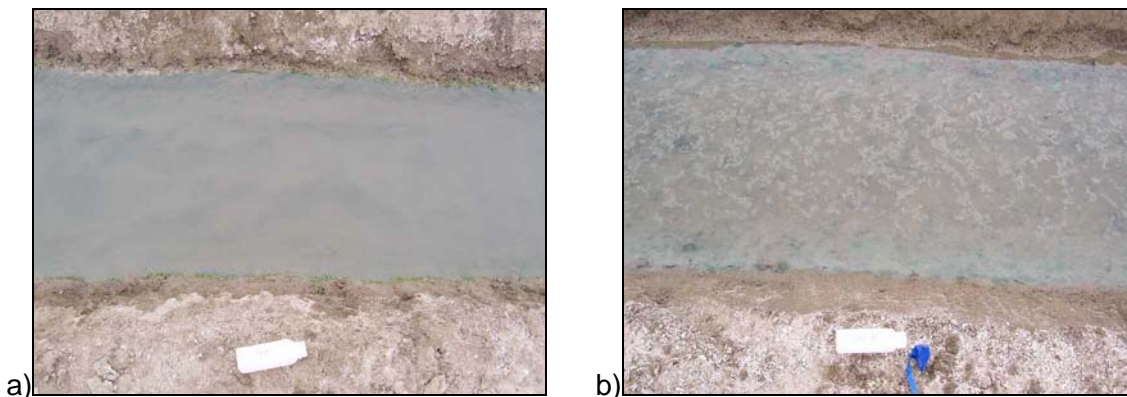
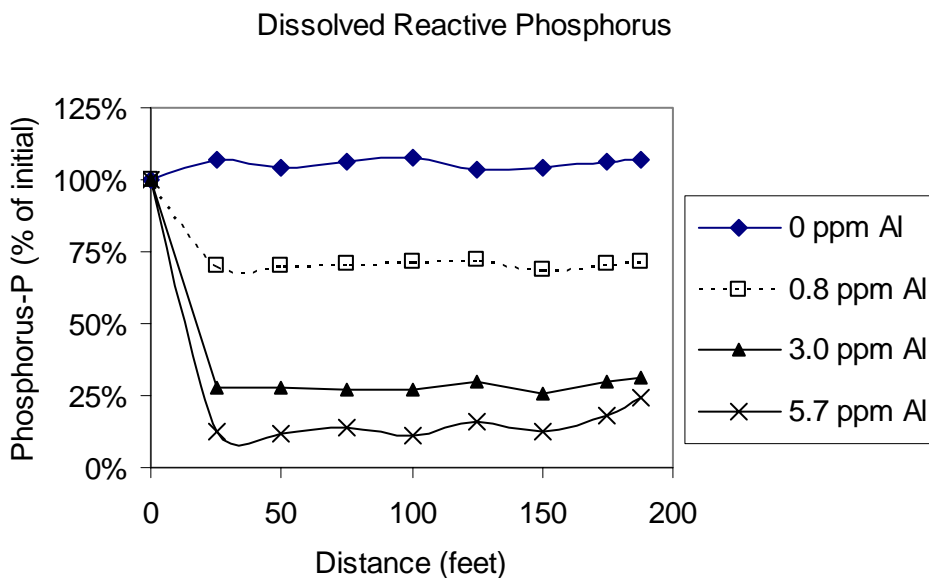


Figure 11. Dissolve reactive phosphorus concentrations in response to varying alum-Al additions on 2/5/04.



Visual observations of alum floc forming but not settling are reinforced by data presented in Figure 12 and Figure 13. The difference between treated and untreated (additions of 7 versus 0 mg Al/L) equilibrium turbidities seen in Figure 12 is much smaller than that seen in the jar tests done in Task 6. Again, discrepancies in mixing energy (G values) may be at fault; the ditch may be much more turbulent a settling environment than an undisturbed jar tester.

Figure 13 shows that water equilibrated with alum treatments still had elevated Al concentrations relative to the 0 ppm Al treatment even as it flowed out of the ditch. Comparing

the 5.7 ppm alum-Al injection rate to the measured 4.3 ppm Al concentration at the outflow suggests that only 25% of the alum-Al settled in the ditch while 75% of it flowed out. Since the mean, field-filtered Al concentration was 14% of the raw water Al concentration (data not shown), 61% of the alum-Al must have left the ditch in the form of un-settled floc.

Figure 12. Decreases in percent initial turbidity with increasing alum additions on 2/5/04.

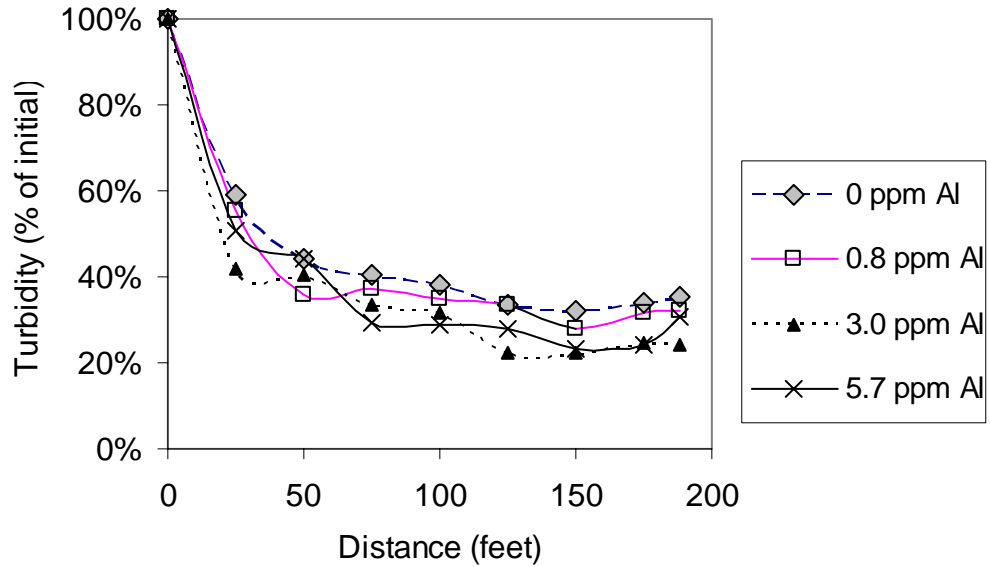
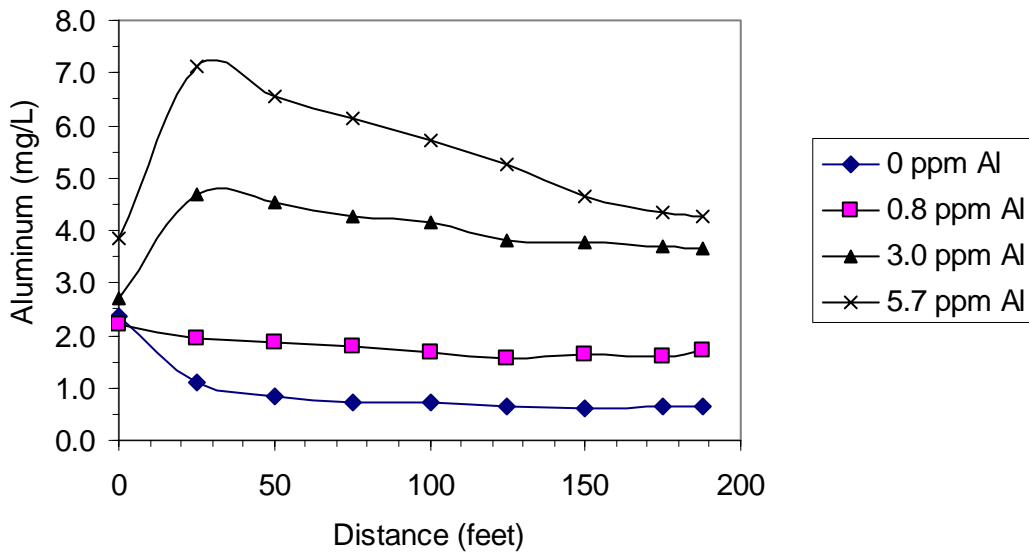


Figure 13. Raw water aluminum concentrations on 2/5/04.



Conclusions

Alum performed as hypothesized in preliminary simulation drainage ditch trials. Significant removals of P_T , P_S , and Turbidity were accomplished in all trials. However, as long as a considerable portion of the alum floc neither settles nor is physically removed, P_T concentrations will remain elevated in these ditch alum trials. The next step in our work is to improve alum floc settling by first testing anionic then, possibly, cationic polymers. Failing these attempts, we should consider methods for the physical removal of light floc like skimming, filtering, dissolved air floatation, or some combination of these methods.

Task 9. Conduct CEP treatment trials (0% complete)

During the winter months, fish cannot be used to harvest algal production due to low temperature. Trials using chemical flocculants and polymers to remove phosphorus and, potentially, selenium will be performed during winter months. Metal salts and polymers will be injected via a chemical mixing chamber submerged in the water-polishing zone of the CEP. Sampling will mimic that of the ditch-scale trials and last for two to three days. With work on the CEP completed (as noted in Task 5.3) and receipt of bulk polymer samples from GE-Betz (as of 3/29/04), we can embark on these trials starting next quarter.

Subtask 9.1. Conduct studies of the effects of seasonal temperature and sunlight variation on CEP treatment efficiency.

Water quality measurements in the CEP have been monitored. The following daily and weekly parameters are being measured: CO_2 additions, algal removal rates, algal productivity, Secchi disc depth, pH, O_2 , TSS, VSS, temperature, and phosphorus and nitrogen levels. The initial portion of this long-term data set will be presented in the next quarterly report.

Subtask 9.4. Evaluate the use of automatic algae removal belts in three existing 0.33 acre CEP units for algal harvest/control using sequencing batch reactors (SBR's) containing filter-feeding fish.

Our research associates at Clemson University are re-configuring the algal harvest zones of four 100 m² prototype CEP units. These modifications will permit studies to be conducted using multiple groups of tilapia in each CEP unit, in order to evaluate the concept of providing two compartments of tilapia for algae removal and a third compartment of tilapia that would be provided with a high carbohydrate diet. Periodically, each group of tilapia would be rotated through the high carbohydrate diet compartment, in order to: 1) provide for increased growth of

the tilapia (yielding a valuable product), 2) insure high health of the captive stock, 3) minimize the effects of extended "starvation periods" during very low algal concentrations in the polishing zone, and 4) provide an economical source of carbon dioxide (from fish respiration) for re-carbonation of the CEP algal culture. Studies will be conducted to determine the optimal cycle time between the feed treatments, and the overall nutrient removal rates that can be achieved through this process. In addition, total fish stocking requirements, biomass production rates, and the effects of fish size and algal species will be evaluated.

Task 10. Monitor biological Se-uptake and evaluate CEP for Se-removal (43% complete)

Introduction

Any water treatment technology which concentrates nutrients for ultimate removal from the system can potentially bioaccumulate toxic compounds that could effect the usefulness of the concentrate. There is some concern that selenium, which is present in low levels in the Salton Sea tributaries, could become concentrated in the food chain. We have begun to monitor the levels of selenium and other analytes in these rivers and the degree to which their levels may be reduced in the CEP system.

Methods

Bulk water samples were collected from the Alamo, New, and Whitewater Rivers and the CEP Algae Zone (see Table 5).

Table 5. River and CEP water sampling sites.

Site	Location
Alamo River	Eddins Rd. (Route S30) bridge
New River	Gentry Rd. (Route S30) bridge
Whitewater River	Kent SeaTech Fish Farm, CEP Inflow
CEP Algae Zone	Kent SeaTech Fish Farm, CEP Algae Zone

Water samples were appropriately acidified and transported back to UC Riverside and refrigerated. Samples were brought to room temperature, well mixed, sub-sampled, and syringe filtered <0.45 μm (Fisherbrand Membrane) as needed. In 10 ml plastic mailing tubes, 0.5 ml of sample water and 0.3 ml of 0.2 M potassium persulfate were combined and heated for 20 min. to digest organic Se (Zhang et al. 1999). Once acidified to 0.6 M with HCl, they were run on a Varian Hydride Generation Atomic Absorption (AA) Spectrometer for total As, Fe, and Se concentrations. Aluminum concentrations were measured with a Plasma Quad ICPOES (Perkin Elmer, Wellesley, MA). Turbidity, ammonia, nitrate, and phosphorus samples were prepared and analyzed as in Task 6. Titrated alkalinity and pH were determined using an Orion EA 920 pH meter. EC was measured in the lab with a YSI 3200 Conductivity Instrument.

Results and Discussion

In order to better understand the water chemistry in which potentially elevated Se concentrations occur, we decided to perform a variety of analysis on water samples. The following is a brief summary of the most notable observations one can make from Table 6.

During the sampling period, all three rivers were above the California Central Valley Grassland Marshes monthly average TMDL of 2 ppb Se. Even though the CEP should now be in equilibrium with it's WR inflow source, it's Se concentration lies below that of the WR and within the limits of this TMDL. Therefore, it is probable that Se is removed by bioflocculation and settling and/or volatilization from the CEP.

Table 6. Fall/Winter '03/'04 conditions in the Salton Sea's tributary rivers.

	Ammonia-	Nitrate-	Dissolved Reactive Phosphorus-	Total Phosphorus-	Al	Fe	TSS
	N	N	P	P			
	------(mg/L)-----						
Alamo R.	1.2	6.6	0.7	1.0	1.293	4	190
New R.	10.9	2.6	2.4	2.6	0.903	13	200
Whitewater R.	2.0	20.9	1.5	1.9	0.250	NA	10
CEP-Treated Whitewater R.	1.8	9.3	0.3	0.6	0.323	NA	56

	As	Se	Alkalinity to pH 4.4	pH	EC	Turbidity	Temp.
	(ug/L)	(ug/L)	(mgCaCO3/L)		(uS/cm)	(NTU)	(deg. C)
Alamo R.	4.3	6.3	267	7.4	3404	145	NA
New R.	4.5	3.1	379	7.3	7030	83	NA
Whitewater R.	1.9	2.5	215	7.4	2111	77	17
CEP-Treated Whitewater R.	4.5	1.5	222	7.3	1793	31	NA

Samples were taken between 10/13/03 and 2/3/04. Ammonia-N, Nitrate-N, and DRP values are averages from samples of filtered water (n=1 for Alamo R. and New R., n=3 for Whitewater R). TSS, Turbidity, EC, pH, and Temperature were measured on raw water.

Red indicates suspect data - needs to be re-run.

Task 11. Determine the effects of turbidity in a CEP (0% complete)

A model scale (1,000 gallon) CEP algal channel was developed for the testing of the effects of increased turbidity on algal growth (see Photo 8). This work will be initiated in July, 2004.

Photo 8. Model scale CEP.



Task 12. Prepare cost projections (0% complete)

Cost projections for the technologies evaluated in this project will be prepared starting in July 2004.

Task 13. Quarterly, Draft and Final Reports (20% complete)

7.1 Quarterly Reports

We will ensure that the contract requirements are met through completion of quarterly status reports submitted to the Contract Manager by the 10th of the month following the end of the calendar quarter and through regular communication with the Contract Manager. The progress reports shall describe activities undertaken and accomplishments of each task during the quarter, milestones achieved, and any problems encountered in the performance of the work under this contract. The description of activities and accomplishments of each task during the quarter shall be in sufficient detail to provide a basis for payment of invoices and shall be translated into percent of task work completed for the purpose of calculating invoice amounts.

7.2 Draft Report

Starting in October, 2004, a draft report will be prepared that includes a list of products of the tasks listed above. The report shall include the following narrative sections: 1) A brief introduction section including a statement of purpose, the scope of the project, and a description of the approach and techniques used during the project. 2) A list of task products previously submitted as outlined in the Schedule of Completion. 3) Any additional information that is deemed appropriate by the Project Director.

7.3 Draft submission

In January, 2005, copies of the draft report will be submitted to the Contract Manager for review and comment.

7.4 Corrections and final draft submission

In February and March of 2005, a final report will be prepared that addresses, to the extent feasible, comments made by the Contract Manager on the draft report. We will submit one reproducible master and two copies of the final project report to the Contract Manager for review and acceptance.

References

- Al-Layla and E. J. Middlebrooks. Effect of Temperature on Algal Removal from Wastewater Stabilization Ponds by Alum Coagulation. *Water Research* 9 873-876.1975.
- Aly S.M. and Letey J. 1988. Polymer and water quality effects on flocculation of montmorillonite. *Soil Science Society of America Journal* 52: 1453-1458.
- Barvenik F.W. 1994. Polyacrylamide characteristics related to soil applications. *Soil Science* 158: 235-243
- Hammer, M. J. and M. J. Hammer. *Water and Wastewater Technology*. 3rd ed. Prentice Hall. Columbus, OH. 1996.
- Greenberg A.E., L.S. Clesceri, and A.D. Eaton, eds. 1992 *Standard methods for the examination of water and wastewater*. 18th Edition. American Public Health Association.
- Malik and Letey, J. Adsorption of Polyacrylamide and Polysaccharide Polymers on Soil Materials. *Soil Science Society of America Journal*. 55:380-383. 1991.
- McGarry. M. G. Algal Flocculation with Aluminum Sulfate and Polyelectrolytes. *Journal of Water Pollution Control Federation*. (42) 5 Part II. 1976.

Milward C.G. and Kluckner P.D. 1989. Microwave digestion technique for the extraction of minerals from environmental marine sediments for analysis by inductively coupled plasma atomic emission spectrometry and atomic absorption spectrometry. *Journal of Analytical Atomic Spectroscopy* 4: 709-713.

Zhang Y., Morre J.N., Frankenberger W.T. Jr. 1999. Speciation of soluble selenium in agricultural drainage waters and aqueous soil-sediment extracts using hydride generation atomic adsorption spectrometry. *Environmental Science and Technology* 33: 1652-1656.