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## **EFFECTS OF ALUM ON THE QUALITY OF AQUACULTURE EFFLUENTS IN SETTLING PONDS**

**Martha Rowan<sup>1</sup>, Amit Gross<sup>2\*</sup> and Claude E. Boyd<sup>3</sup>**

<sup>1</sup> *Department of Zoology, 207 Research Station Road, North Carolina State University, Plymouth, North Carolina 27962, USA*

<sup>2</sup> *Department of Environmental Hydrology and Microbiology, Institute for Water Sciences and Technologies, Jacob Blaustein Institutes for Desert Research, Ben Gurion University of the Negev, Sde Boker Campus, 84990 Midreshet Ben Gurion, Israel*

<sup>3</sup> *Department of Fisheries and Allied Aquacultures, Auburn University, Auburn, Alabama 36849, USA*

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### **Abstract**

The effectiveness of alum (aluminum sulfate) in reducing the concentrations of potential pollutants in pond effluents was investigated in catfish production ponds. Application of alum at 50 mg/l to water remaining in ponds immediately after seining for harvest did not generally result in significantly greater removal of nutrients and solids than did settling alone, although removal rates of some variables were initially higher in the alum treated ponds. Within four hours of seining in both alum treated and untreated ponds, there was removal of more than 85% of total suspended solids, 75% of total phosphorus, 72% of turbidity, and more than 40% of biochemical oxygen demand and chemical oxygen demand. Concentrations of soluble reactive phosphorus decreased after 48 h, but total ammonia nitrogen was not removed. Alum may be more effective in improving water quality in settling ponds if it is applied after the initial sedimentation has occurred.

### **Introduction**

Standard pond management practices of commercial catfish farmers in the southeastern USA include the use of fish production ponds for several years without draining. Ponds may be partially drawn down to facili-

tate seining or repair embankments, however ponds are completely drained on average once every 6.1 years (APHIS, 1997). Effluent from concentrated aquatic animal production (CAAP) facilities is considered point source

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\* Corresponding author. Email: amgross@bgumail.bgu.ac.il

pollution by the United States Environmental Protection Agency (USEPA) and is subject to regulation by the National Pollution Discharge Elimination System (NPDES). Of concern is the pollution potential of the nutrients and organic matter contained in the effluent when the ponds are drained, and the impact of the effluent on receiving streams. Previous studies have characterized channel catfish pond effluent and shown that the first 50-80% of the water drained is similar in quality to normal pond water (Schwartz and Boyd, 1994a,b). Pond water discharged after the seining phase has high levels of nutrients and suspended solids. Approximately 50% of the potential pollutants in pond water are contained in the last 15-20% of the water drained from the pond (Schwartz and Boyd, 1994a). Treatment of this last fraction of effluent in settling ponds before reuse or discharge has been recommended as an effective way to improve the quality of pond effluents and reduce their impact on the environment (Schwartz and Boyd, 1994b; Seok et al., 1995; Boyd and Tucker, 1998). Laboratory studies of sedimentation of synthetic channel catfish pond effluents demonstrated that a settling time of eight hours was sufficient to reduce total suspended solids and total phosphorus by 75%, and turbidity and BOD by more than 40% (Boyd and Tucker, 1998).

The use of separate settling ponds to treat aquaculture effluent can be problematic on commercial fish farms because of land requirements and construction costs (Boyd and Queiroz, 2001). Existing ponds could be converted to settling ponds, but this would result in a loss of production capacity. Holding pond water for several hours or days in production ponds before discharging it into the environment has been suggested as a practical way to mitigate effluent impact (Seok et al., 1995) and is a procedure that has been suggested as an aquaculture best management practice.

Alum (aluminum sulfate) has long been used in aquaculture to clear turbidity in fish ponds (Boyd, 1979; Boyd and Tucker, 1998), in potable and waste water treatment systems as a coagulant (Faust and Aly, 1983), and in

lake restoration to reduce internal loading of phosphorus (Cooke et al., 1993). Its utility in precipitating and inactivating phosphorus in aquaculture production ponds has also been investigated (Masuda and Boyd, 1994a). When alum is added to water, a non-toxic aluminum hydroxide floc forms that has high coagulation and phosphorus adsorption properties. As this floc settles to the pond bottom it also removes some organic particles through coagulation and entrapment. Application of alum to fish production ponds after seining may enhance the settling of solid particles and increase the removal of potential pollutants from the pond water.

This study was conducted to determine the effectiveness of channel catfish culture ponds used as settling basins in reducing concentrations of nutrients and solids in the effluent and to determine if application of alum will improve effluent quality.

#### Materials and Methods

Eight 0.04-ha earthen ponds located at the Auburn University Fisheries Research Unit containing approximately 600 kg of channel catfish (15,000 kg/ha) were used in this study. The ponds have an average depth of 0.9 m and are equipped with internal, swivel-type standpipes. Auburn is located on the Piedmont Plateau in Alabama and soils are acidic and highly leached. Typical particle size composition of these pond soils is 34.4% sand, 24.0% silt, 41.6% clay, and the soil contains 4-6% organic matter (Boyd and Tucker, 1998).

Four ponds were randomly assigned to the treatment group and four ponds were used as controls. The ponds had been stocked in the spring and managed according to standard commercial pond management practices until the fall harvest. Fish were fed to satiation during the culture period with a 32% protein floating pellet, and feeding rates peaked at 100 kg/ha 3 weeks before harvest. Nightly aeration with 0.37-kW vertical pump aerators (Air-o-Later Corp., Kansas City, Missouri) maintained dissolved oxygen concentrations above 3.0 mg/l during the culture period.

Ponds were drained to approximately 60% of full volume in preparation for harvesting by seining. The volume of water remaining in each pond at this time was determined by measuring water depths in approximately 50 locations, and the calculated volumes were used to determine the amount of alum to be applied to four of the ponds. Each pond was seined twice with a 19-mm mesh nylon seine equipped with a mudline, and 90-95% of the fish were removed.

Within 10 min after the ponds were seined, commercial grade alum was dissolved in pond water and broadcast over the treatment pond surfaces by hand to result in pond water concentrations of 50 mg alum/l (4.55 mg Al<sup>3+</sup>/l). This application rate was selected based on the range of alum floc points (the concentration of alum required to cause a 50% decrease in turbidity) of 15-40 mg/l determined by Masuda and Boyd (1994a) for 11 catfish pond waters in Auburn.

Water samples were taken from each pond at the standpipe before and after seining (before alum application) and after 1, 2, 4, 8, 12, 24, and 48 h. After 72 h, the standpipes were pushed all the way down to completely drain the ponds. When the water depth was approximately 15 cm, the remaining fish were removed by hand by workers wading in the ponds (scrapping). Water samples were taken immediately before and after scrapping.

The following water quality parameters were measured in each sample: total nitrogen (persulfate digestion followed by nitrate determination with NAS reagent; Gross and Boyd, 1998), total ammonia nitrogen (phenate procedure), total phosphorus (persulfate oxidation and ascorbic acid method), soluble reactive phosphorus (ascorbic acid method), chemical oxygen demand (potassium dichromate-sulfuric acid oxidation; Boyd and Tucker, 1992), biochemical oxygen demand (standard 5-day test), total suspended solids (filtration through glass fiber filter followed by gravimetry), turbidity (nephelometry) and chlorophyll *a* (acetone methanol extraction; Pechar, 1987). Unless otherwise indicated, analyses followed protocols outlined in Eaton et al. (1995).

Jar tests were conducted in the laboratory to determine the amount of alum that would be required to precipitate 75% of the phytoplankton from the pond water (as estimated by chlorophyll *a* concentrations). Water from the ponds that were to be treated in the field portion of this study was placed in 2-l glass jars and treated with alum. Chlorophyll *a* was measured before treatment and after 4 h. Four different alum doses were used for water from each pond, with ranges of 50-500 or 250-1,500 mg alum/l. The appropriate dosage range for each pond was selected by treating a small (separate) volume of water with different concentrations of alum solutions and visually estimating decreases in phytoplankton abundance and turbidity.

Statistical significance of differences in variables between treatments was determined by *t* tests at the 5% level. All statistical analyses were performed with SigmaStat v2.03 Statistical Software (SPSS, 1997).

### Results and Discussion

The water quality variables in the settling ponds before and after harvest are presented in Table 1. Although mean concentrations of the initial (before seining) water quality variables appeared to be higher in treatment ponds than in control ponds, these variables did not differ because of high variability between replicates ( $p > 0.05$ ). Seining disturbed and suspended the soft surface mud that was on the pond bottom and resulted in substantial and rapid increases in concentrations of most water quality variables. Concentrations of most variables decreased significantly in the first hour of sedimentation in both the alum treated and control ponds, with little change after four hours. Total phosphorus, turbidity, total suspended solids, biological oxygen demand and chemical oxygen demand declined in concentrations within the first hour after seining to levels similar to the pre-seining concentrations, as expressed in the high removal rates (Figs. 1 and 2). After the initial decrease, concentrations of these variables did not change significantly for the following 48 hours. Concentrations of total nitrogen also decreased after seining (Table 2), although at

Table 1. Water quality variables in channel catfish settling ponds at selected times after harvest. Alum ponds were treated with 50 mg/l aluminum sulfate immediately after seining. Values are means±standard errors.

Variable (mg/l)		Before seining	Immediately after seining	4 h after seining	48 h after seining	Before scrap	After scrap
Total phosphorus	Control	0.68±0.21	3.53±0.59	0.80±0.22	0.46±0.14	1.29±0.29	3.45±0.49
	Alum	0.84±0.11	4.02±0.83	0.88±0.19	0.75±0.01	0.72±0.04	2.59±1.64
Total nitrogen	Control	8.49±2.71	10.04±0.52	9.46±2.09	5.71±1.02	6.82±1.36	9.13±0.87
	Alum	8.66±1.09	10.23±0.78	8.44±0.80	6.16±0.27	7.24±0.86	13.06±0.10
5-day biological oxygen demand	Control	11.3±1.8	28.8±7.88	16.7±3.88	16.1±4.1	32.3±7.43	113.8±21.3
	Alum	16.4±1.3	40.0±3.2	17.4±2.05	21.5±5.3	34.85±2.02	100.0±30.7
Chemical oxygen demand	Control	53.8±10.3	88.0±16.2	56.5±13.1	51.8±12.1	77.3±20.0	1,066±323
	Alum	87.8±25.9	182.0±17.9	85.5±16.8	86.5±17.0	111.0±30.4	650±495
Total suspended solids	Control	68.3±16.1	1,174±264	134.4±30.4	43.7±9.0	102.2±44.1	11,900±4,574
	Alum	115.6±25.8	2,554±663	192.7±57.4	114.6±24.7	105.7±46.9	4,415±77.8
Chlorophyll a	Control	280.1±120.3	355.2±121.8	382.0±142.0	166.3±39.4		
	Alum	570.9±203.8	1,067±228.5	629.6±196.9	558.2±136.5		
Turbidity (NTU)	Control	74±21	634±51	172±28	72±13	118±62	964±114
	Alum	96±25	742±19	206±50	171±36	135±16	694±144
Total ammonia nitrogen	Control	2.06±0.48	3.52±0.70	3.68±0.75	3.63±0.95	2.21±0.61	3.64±0.19
	Alum	0.87±0.43	1.99±0.54	2.72±0.88	1.79±0.59	0.98±0.35	1.47±0.62
Soluble reactive phosphorus	Control	0.018±0.004	0.029±0.004	0.076±0.025	0.010±0.005	0.013±0.010	0.020±0.006
	Alum	0.016±0.002	0.036±0.014	0.057±0.067	0.036±0.023	0.013±0.017	0.150±0.093

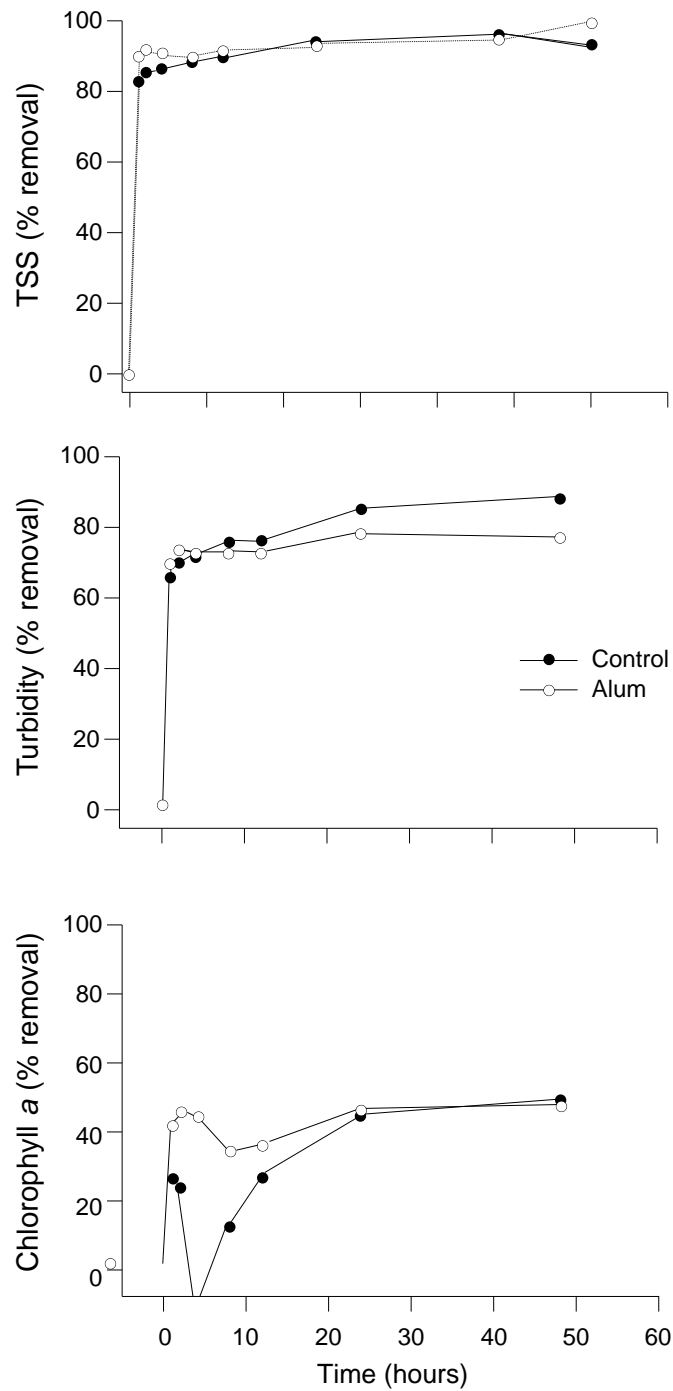


Fig. 1. Percent removal of total suspended solids, turbidity, and chlorophyll a in aquaculture ponds with alum treatment or settling.

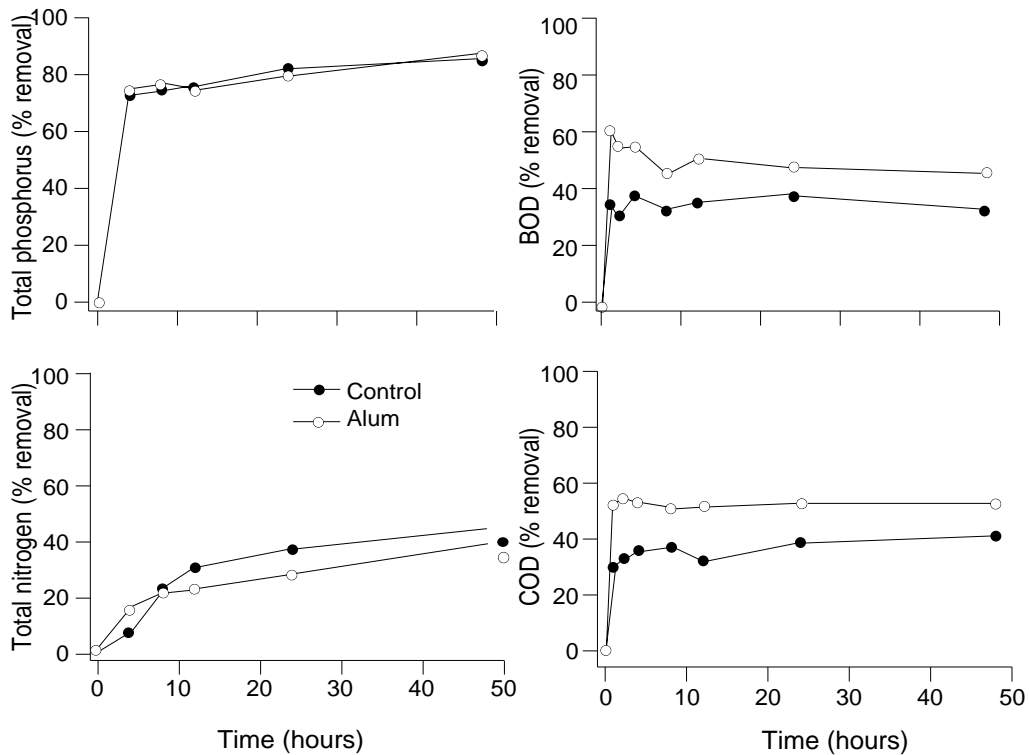


Fig. 2. Percent removal of total nitrogen, total phosphorus, chemical oxygen demand and biological oxygen demand in ponds with alum treatment or settling.

a slower rate (Fig. 2), and ultimately dropped to concentrations lower than the pre-seining levels. The increase in chlorophyll *a* concentration immediately post seining was probably caused by an interference of high concentration fine suspended solids that could not be filtered out. After 48 hours of settling, the levels of chlorophyll *a* were similar to pre-seining levels in the control and treated ponds. Soluble reactive phosphorus and total ammonia nitrogen both continued to increase after seining and peaked in concentration after 2-4 hours (Fig 3).

Alum treatment did not generally result in significantly greater removal of nutrients and solids than did settling alone, although removal rates of some variables were initially higher in the treated ponds. The only statistically significant difference between alum and control pond

removal rates was in BOD after the first hour. Values of BOD and COD after seining quickly decreased more than 50% in ponds treated with alum and did not change in the next 48 hours; control ponds exhibited a similar pattern to approximately 35% with no further change in concentration. Concentrations of TSS and turbidity were reduced after one hour of settling by 90% and 69%, respectively, in alum treated ponds and 83% and 65% in control ponds. After 48 hours, 95% of TSS had settled out in both sets of ponds. Usually, COD and BOD are related to the solid phase matter in aquaculture ponds (i.e., plankton and feed residues). Interestingly there was no similarity between the COD and BOD removal patterns to those of the TSS. It is likely that, after seining, the proportion of inorganic particles in the TSS was

Table 2. Chlorophyll *a* removal four hours post alum application. Experiment was done in 4-l jars containing water from fishponds at the Auburn University research station.

<i>Alum dose (mg/l)</i>	<i>Chlorophyll a prior to alum application (µg/l)</i>	<i>Chlorophyll a 4 h post application (µg/l)</i>	<i>Reduction (%)</i>	<i>Average (%)</i>
50	87	49.0	43.7	59.4
50	135	16.4	87.9	
50	620	330.0	46.8	
250	278	111.4	59.9	74.6
250	365	61.4	83.2	
250	499	119.4	76.1	
250	1164	240.1	79.4	
500	87	8.4	90.3	89.3
500	135	16.4	87.9	
500	365	27.3	92.5	
500	499	80.0	84.0	
500	620	19.7	96.8	
500	1164	179.5	84.6	
1000	365	21.9	94.0	91.4
1000	499	52.9	89.4	
1000	1163	106.3	90.9	
1500	365	14.1	96.1	93.0
1500	499	47.3	90.5	
1500	1163	89.0	92.3	

much greater than the organic particles, which masked their contribution to the TSS. Therefore, differences in TSS between treatments were not found. The greater percent decrease in BOD and COD levels apparent in treated ponds is likely in part a reflection of the relatively higher values of these variables at time=0 in comparison to those levels measured in the control ponds. Mean time=0 COD

concentration was significantly higher ( $p < 0.05$ ) in the treated ponds, and because at this point alum had not yet been applied to the ponds, the difference was related not to the treatment but to the vagaries of seining. In both treated and untreated ponds the values of COD quickly returned to pre-seining concentrations and stabilized at those levels. BOD values showed similar patterns of decrease.



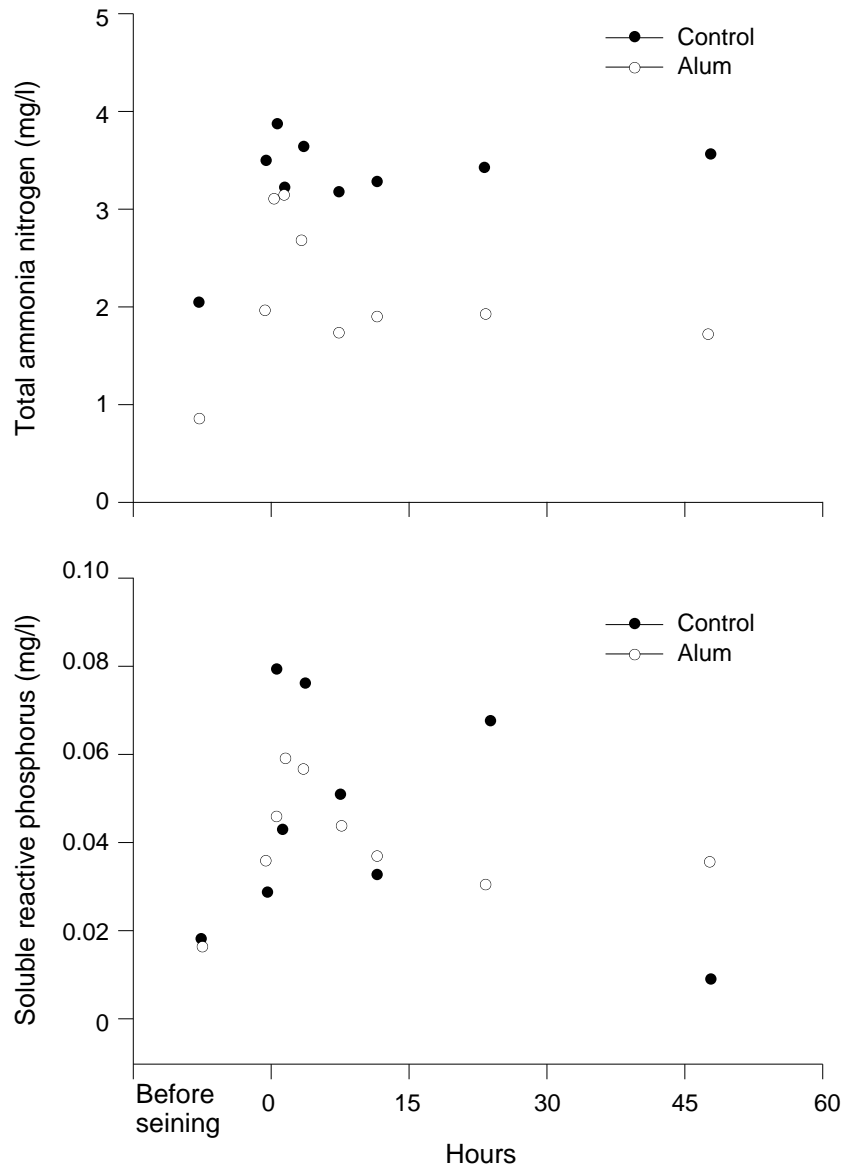


Fig. 3. Total ammonia nitrogen and soluble reactive phosphorus concentrations in alum treated and control settling ponds over 48 h.

Total phosphorus decreased 75% after four hours of settling in both treated and untreated ponds, but TN decreased only 15% and 7%, respectively, during the same time period. Additional settling time did not sub-

stantially increase the removal of TP, but after 48 hours TN was reduced in both sets of ponds by approximately 40%. Although the reasons for the continuous N removal were not tested, it is possible that it was due to

enhanced denitrification. Reduction of the water volume and suspension of suspended solids and bottom organic matter after seining might have reduced the dissolved oxygen concentration in the water and created favorable conditions for denitrification. Total ammonia nitrogen accounted for 25-30% of TN and was not removed in either treated or control ponds. Dissolved substances such as TAN and SRP are released from the anaerobic soil pore water after disturbance of the oxidized sediment-water interface. Masuda and Boyd (1994b) found that the pore water of catfish production ponds contained much higher levels of SRP and TAN than did the pond water. Weakly bound ammonium and SRP can also be rapidly desorbed from resuspended soil particles (Reddy et al., 1996). Concentrations in pond water of both TAN and SRP would decrease over time from phytoplankton uptake, and nitrification would also reduce TAN. The relatively higher amount of phytoplankton in the treated ponds could account for the lower TAN in those ponds.

Substantially higher application rates of alum would have been necessary to precipitate significant amounts of phytoplankton. In jar tests of these pond waters, in only one of the samples was 50 mg alum/l sufficient to reduce chlorophyll *a* concentrations by at least 75% (Table 2). Pond waters varied considerably and the required alum concentrations for 75% chlorophyll *a* reduction ranged from 50 to 500 mg/l. The average chlorophyll *a* removal at the alum dose of 50 mg/l was 59.4%. The average alum concentration required to remove 75% of the chlorophyll *a* was 250 mg/l. Approximately 90% removal was achieved by application of 500 mg/l alum and higher concentrations did not result in significantly higher removal rates. In ponds, it would probably take more than 250 mg/l to remove 75% of the chlorophyll *a* as wind and uneven distribution affect the removal efficiency. Chlorophyll *a* removal would require large quantities of alum, which is expensive and may have negative environmental effects such as a decrease in pH and contamination by aluminum and sulfur.

As ponds were drained in preparation for

removal of the remaining fish, the fish became concentrated in the smaller volume of water and the resulting bioturbation caused increased levels of nutrients and solids in the water. Alum treated ponds exhibited less of an increase in most variables than did the control ponds. Levels of BOD, TP and TSS doubled in the untreated ponds, probably because of the resuspension of settled phytoplankton and other organic and inorganic particles. The alum floc that settled to the pond bottoms may have limited this resuspension in the treated ponds. Munsiri et al. (1995) found that the upper flocculent layer in fishponds was approximately 50% organic matter. Water quality significantly deteriorated during pond scrapping and most water quality variables rose to extremely high levels. These pond bottoms were very soft and at times workers sank in mud up to 0.75 m deep while they were retrieving the remaining fish.

Patterns and magnitudes of decrease of concentrations of water quality variables were similar to those found by Boyd and Tucker (1998). The greatest proportion of potential pollutants was removed within the first hour of settling with little change after four hours. There were no significant differences in percentage removal between one hour and 48 hours of settling for any of the water quality variables except for TN. Patterns of removal by sedimentation of pollutants and solids are comparable in the control and alum treated ponds. Application of alum immediately after seining resulted in a somewhat greater removal rate of some pollutants during the first hours of settling, but did not significantly improve water quality. Coagulants such as alum assist in the aggregation and more rapid settling of small particles. Since alum works quickly and has no residual effect, it would be beneficial to test its effectiveness in aquaculture ponds by applying it after the first hour of settling has occurred. At that point, concentrations of most of the pollutants will have decreased substantially, and alum added at that time would probably act on suspended substances more resistant to settling and on soluble phosphorus desorbed from particles. If ponds are to be completely emptied of

water, a short settling period after seining and before discharge will permit removal of a substantial proportion of potential pollutants from the pond water. The remaining water should then be discharged very slowly to prevent resuspension of sediment.

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