Lakeside Lake Bench-Scale Testing with Aluminum Sulfate

David Walker, PhD.

Methods

Samples were obtained from Lakeside Lake, reclaimed water (prior to entering the lake), and well PK-09 (prior to entering the lake), for testing with aluminum sulfate (alum) to determine the potential use of alum in alleviating problems associated with eutrophication.

Lake samples were collected on 09/04/06 from the surface of site SCLAK-B (North Site). Turbidity due to recent storm events and subsequent runoff via Atterbury Wash into the lake was pronounced. Algal biomass was low likely due to light limitation in addition to dilution and flushing of lake water. Algal biomass, however, had been relatively low leading up to these runoff events.

Samples were collected from well PK-09 and the reclaimed water line prior to entering the lake on 09/12/06. Both samples were collected in acid-washed and sterilized, 10 liter plastic carboys. Reclaimed water was allowed to run for approximately 45 minutes prior to collection. Water from well PK-09 initially came out orangish-brown indicating rust contamination. The water was allowed to run for approximately 2 hours before after which the discoloration was gone and water was collected.

At the lab, water was placed into a 4-liter churn splitter and homogenized prior to transferring into 5, acid-cleaned, 1-liter beakers. Liquid alum was purchased from Orca Water Technologies LLC. The solution supplied was 46 ± 3% alum by weight, 7.9 ± 0.5% Al_2O_3, 4.2 ± 0.3% Al, and 0.3 ± 0.2% sulfuric acid with a specific gravity of 1.32 ± 0.01.

The alum mixture was diluted with nanopure water and the following alum doses were added to each beaker with a digital pipette to derive our aluminum (not alum) concentrations per liter of sample water.

0.1 mL alum = 0.13 ppm Al
0.4 mL alum = 0.52 ppm Al
0.8 mL alum = 1.04 ppm Al
2.3 mL alum = 2.99 ppm Al
3.9 mL alum = 5.08 ppm Al

Samples were stirred using a 6-paddle, Phipps & Bird floc jar apparatus at approximately 100 rpm for 5 minutes, 50 rpm for 6 hours, and then were allowed to settle for 18-20 hours. All samples except for total aluminum were collected off the supernatant being careful not to disturb the floc. After these samples were obtained, the paddles were turned back on at 100 rpm to once again homogenize the sample for collection of the total aluminum sample.

Background

Free Al^{+3} ions are formed when aluminum sulfate, $Al_2(SO_4)_3$ is added to water and these ions are quickly attached to six water molecules to form $Al(H_2O)_6^{+3}$. Several hydrolytic species are next formed due to a successive loss of protons to surrounding water molecules (Harper 1990).

$$Al(H_2O)_6^{+3} + H_2O \rightleftharpoons Al(H_2O)_5OH^{+2} + H_3O^{+}$$

$$Al(H_2O)_5OH^{+2} + H_2O \rightleftharpoons Al(OH)_2(H_2O_4)^{+} + H_3O^{+}$$

$$Al(OH)_2(H_2O_4)^{+} + H_2O \rightleftharpoons Al(OH)_3(H_2O)_{3(s)} + H_3O^{+}$$

The final product, $Al(OH)_3(H_2O)_{3,}$ is the alum precipitate or "floc" and is usually written as $Al(OH)_3$.

Under alkaline conditions an additional reaction can occur:

$$Al(H_2O)_6^{+3} + 4H_2O \rightleftharpoons Al(OH)_4^{-} + 4\ H_3O^{+}$$

There are three mechanisms of phosphorous removal by alum in water (Cooke & Kennedy, 1981, Harper 1990);

- from the formation of insoluble $AlPO_4$,
- by sorption on the surface of the $Al(OH)_3$ floc and,
- by entrapment of phosphorous-containing particulate matter in the $Al(OH)_3$ floc.

This same mode of action by alum to remove phosphorous can also significantly increase the settling rate of suspended particulate material from the water column and has even been shown to remove dissolved organic material adding to color of the water. Since this suspended material carries an oxygen demand with it, the effect of removing an essential nutrient for algal growth (P) combined with removing suspended material would likely result in increased dissolved oxygen levels within the water column.

Toxicity

Like many metals, the toxicity of aluminum is not well correlated with levels of total aluminum but is correlated with the biologically-active fraction. The inorganic, monomeric form of aluminum, Al^{+3}, is believed to be the most toxic. Toxicity of aluminum in a waterbody is usually measured as the dissolved fraction of the total and is dependent upon other water quality criteria, especially pH levels. Under typical situations encountered in freshwater environments, the toxic fraction is an extremely small fraction of the total (Livingston et al., 1994). Increasing toxicity is reported in the literature at pH levels below 5.5 and above 8.5.

Numerous studies have been performed to determine the toxicity of aluminum to fishes and have concluded that:

-Surges of labile aluminum during snowmelt and heavy rainfall were potentially lethal to fish eggs and fry (Driscoll et al., 1980)

-At low pH, doses as small as 50 µg/L of aluminum have decreased growth and survival of cutthroat trout (Woodward et al., 1989) small-mouth bass (Kane and Rabeni, 1987), and post-larval white suckers (Baker and Schofield, 1982).
-Toxicity of aluminum varies with pH and life history stage of fish.
-The extent of aluminum toxicity appears to be dependent on pH levels, total concentration, and the speciation of dissolved aluminum.
- The mechanism of toxicity to fish is likely due to the inability of fish to maintain their osmo-regulatory balance as well as respiratory problems associated with coagulation of mucous on gills.
Toxicity of aluminum on invertebrate species has been conducted following in-lake alum treatments of lakes and has concluded that:
- Acute concentrations of aluminum hydroxide has no acute effect on the chironomid *Tantytarsus dissimulus* but chronic assays were noted at all alum doses (Lamb and Bailey, 1981).
- No indications of short- or long-term toxicity to benthic invertebrates were observed in Horseshoe Lake following an alum treatment (Narf, 1978).

The Environmental Protection Agency based upon a review of the above information, established guidelines for aluminum concentrations for over 20 species of freshwater organisms ranging from algae to aquatic invertebrates to fish. To avoid chronic toxicity to organisms, the EPA has established conservative criteria that the four-day average concentration of dissolved aluminum not exceed 87 µg/L more than once every three years when the ambient pH is between 6.5 and 9.0. Regarding acute toxicity, the criteria states that the one-hour average concentration of dissolved aluminum not exceed 750 µg/L more than once every three years when pH levels are between 6.5 and 9.0.

Results

The best results in the lake samples were obtained between the doses of 1.04 and 2.99 ppm of Al, however, improvement over raw lake water was observed at all doses. Total suspended solids was significantly decreased even at the dose of 0.13 ppm Al. and improved in a dose-dependent manner after this. The samples used for this testing from the lake had high turbidity and low algal biomass so the 24 hour pH levels would likely have been higher in samples obtained during a more typical year. Alum did not significantly reduce any of the nitrogenous compounds but did significantly increase sulfate and decrease total alkalinity again in a dose-dependent manner. Total alkalinity levels within Lakeside, in lieu of any significant runoff from Atterbury Wash, are typically much higher so that the relatively low levels observed at the higher alum doses during this testing, and would typically be much higher. Sulfate levels are always an issue due to the production of hydrogen sulfide and its related toxicity to aquatic organisms, however, if dissolved oxygen levels can be increased and algal biomass decreased through the use of alum, then hydrogen sulfide should not be formed within the lake to any appreciable extent.

The reclaimed water had relatively high levels of both ortho- and total phosphorous in the raw samples so that it required higher doses of alum to bring these levels down. Alum still significantly reduced levels of both ortho- and total phosphorous and, if diluted with water from well PK-09 which had extremely low levels of phosphorus, would likely result in a large decrease in P loading to Lakeside. It seems feasible, based upon these results, that Lakeside could be made to be P-limited resulting in a significant decrease in algal biomass and increase in dissolved oxygen levels.

Another benefit of alum observed in these results is the very significant reduction of suspended solids and turbidity observed in the lake samples. These suspended solids have an associated oxygen demand and removing them from the water column as quickly as possible can only result in increased dissolved oxygen levels.

Taking the extremely conservative approach of the already-conservative EPA guidelines for dissolved aluminum toxicity of 87 µg/L (0.087 mg/L), this report would recommend dissolved aluminum levels be kept below 75µg/L (0.075 mg/L) at all times. Two doses from within the lake samples, LKS-0.52 and LKS-0.13, exceeded this self-imposed, chronically toxic level when the dissolved aluminum fractions were 180 µg/L at a pH of 7.45 and 100 µg/L at a pH of 7.45 respectively. No levels came close to being acutely toxic.

If alum is to be used in Lakeside, careful and frequent monitoring of in-lake conditions by trained personnel would be essential to ensure no chronic or acute toxicity occurs to aquatic organisms.

Cost

The lowest results that did not cross the upper toxicity level of 0.075 mg/L but still significantly reduced phosphorous and suspended sediment levels within the lake samples was LKS-2.99. This dose was measured at 3.05 mg/L of total aluminum but will be rounded to 3.0 mg/L for this calculation. It is important to remember that dosing of the lake will have to be adjusted throughout the year depending upon phosphorous loading, evaporation, runoff into the lake, amount of seepage, total alkalinity, pH levels, and many different variables which cannot all be taken into consideration in this report. Cost can be calculated either up or down depending upon concentrations that need to be achieved within the lake; however, the 3.0 mg/L range seems like a logical "starting point" given the results of this bench-scale testing. This cost is associated with the amount of liquid alum it would take to get aluminum throughout the entire water column to 3.0 mg/L. Once this level is achieved, maintenance levels would cost far less than this initial estimate. Again, the exact price it would take to maintain a level of 3.0 mg/L depends upon a multitude of variables that are outside the scope of this report. The cost of liquid alum varies regionally but nation-wide seems to (conservatively) be between 10 and 20 cents per pound of alum.

Lakeside is approximately 150 acre feet when full which equals 154,190,000 liters. Liquid alum usually contains 4.3% aluminum. The 3 mg/L dose of aluminum is equivalent to 0.06977 g/L of alum.

0.06977 grams X 154,190,000 L = 10,757,836.3 grams.

10,757,836.3 grams = 23,714 pounds of liquid alum.

23,714 pounds of liquid alum at 10 cents/pound = **$2371**

23,714 pounds of liquid alum at 20 cents per pound = **$4743**

The median cost of adding liquid alum to Lakeside Lake to achieve an aluminum concentration of 3.0 mg/L throughout the water column is **$3557.**

Lakeside Lake Floc Jar Testing Results

Lake Samples Collected from the Surface of Site SCLAK-B on 09/04/06

Sample ID	Total Al (mg/L)	Diss. Al (mg/L)	Ortho-P (mg/L)	Total P (mg/L)	TSS (mg/L)	pH-1 min.	pH-1 hr
Raw Lake Water	<0.01	<0.01	0.32	0.38	52.3	7.78	
LKS-0.13	0.15	0.1	0.2	0.32	14.3	7.16	7.04
LKS-0.52	0.52	0.18	0.12	0.28	9.7	6.8	6.75
LKS-1.04	1.07	0.07	0.08	0.16	6.0	6.58	6.63
LKS-2.99	3.05	0.04	<0.05	0.07	1.1	6.43	6.13
LKS-5.08	5.13	0.03	<0.05	<0.05	<1.0	5.94	6.15

Sample ID	pH-24 hr	Total Alk. (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	Total N (mg/L).	Sulfate (mg/L)
Raw Lake Water		74.2	0.43	0.22	0.73	2.3
LKS-0.13	7.45	69.1	0.39	0.2	0.61	3.56
LKS-0.52	7.45	66.5	0.36	0.2	0.6	8.13
LKS-1.04	7.08	64.0	0.36	0.19	0.62	13.7
LKS-2.99	6.77	36.3	0.35	0.17	0.58	36.6
LKS-5.08	6.38	12.9	0.35	0.15	0.55	58.55

Sample ID	TOC (mg/L)	DOC (mg/L)	Turbidity-24 hr. (NTU's)
Raw Lake Water	7.41	2.85	67.1
LKS-0.13	5.3	2.8	25.0
LKS-0.52	4.99	2.43	26.7
LKS-1.04	4.99	2.11	11.02
LKS-2.99	3.73	2.11	1.83
LKS-5.08	3.61	1.64	1.23

Reclaimed Water
Collected on 09/12/06

Sample ID	Total Al (mg/L)	Diss. Al (mg/L)	Ortho-P (mg/L)	Total P (mg/L)	TSS (mg/L)	pH-1 min.	pH-1 hr
Raw Reclaimed Water	0.16	0.01	2.05	2.07	6.0	7.57	
RE-0.13	0.33	<0.01	1.77	1.75	4.1	7.54	7.54
RE-0.52	0.65	0.07	1.39	1.59	3.0	7.43	7.44
RE-1.04	1.22	0.02	1.24	1.28	2.5	7.34	7.01
RE-2.99	3.24	0.02	0.44	0.48	1.2	7.05	6.97
RE-5.08	5.30	<0.01	0.13	0.23	<1.0	6.77	6.85

Sample ID	pH-24 hr	Total Alk. (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	Total N (mg/L).	Sulfate (mg/L)
Raw Reclaimed Water		170.0	2.72	<0.05	4.08	99.04
RE-0.13	7.56	170.0	2.81	<0.05	4.00	109.24
RE-0.52	7.55	163.4	3.04	<0.05	3.88	113.98
RE-1.04	7.26	157.8	3.12	<0.05	3.57	121.7
RE-2.99	7.16	133.5	3.12	<0.05	3.63	147.21
RE-5.08	7.02	116.2	2.75	<0.05	3.09	176.00

Sample ID	TOC (mg/L)	DOC (mg/L)	Turbidity-24 hr. (NTU's)
Raw Reclaimed Water	1.38	1.13	2.66
RE-0.13	1.36	1.38	0.79
RE-0.52	1.34	1.11	0.35
RE-1.04	1.27	1.16	0.30
RE-2.99	1.21	1.17	0.26
RE-5.08	1.19	1.08	0.17

Well PK-09
Collected on 09/12/06

Sample ID	Total Al (mg/L)	Diss. Al (mg/L)	Ortho-P (mg/L)	Total P (mg/L)	TSS (mg/L)	pH-1 min.	pH-1 hr
Initial (raw Pk-09 water)	<0.01	<0.01	0.03	<0.01	5.3	7.77	
0.13	0.15	<0.01	<0.01	<0.01	3.9	6.81	7.14
0.52	0.48	0.07	<0.01	<0.01	4.0	6.77	7.02
1.04	0.97	0.03	<0.01	<0.01	0.3	6.65	6.89
2.99	2.76	0.03	<0.01	<0.01	<1.0	6.42	6.61
5.08	4.88	0.02	<0.01	<0.01	<1.0	6.21	6.57

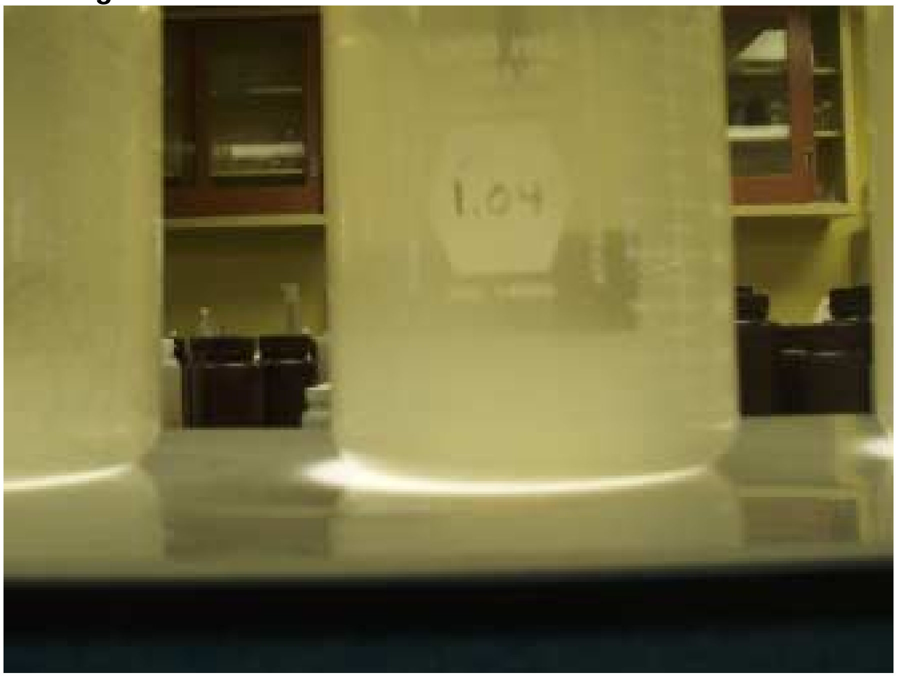
Sample ID	pH-24 hr	Total Alk. (mg/L)	NO3-N (mg/L)	NH4-N (mg/L)	Total N (mg/L).	Sulfate (mg/L)
Initial (raw Pk-09 water)		183.7	14.03	0.12	14.51	26.08
0.13	7.47	160.4	13.12	0.05	13.48	32.05
0.52	7.26	158.8	12.84	<0.05	13.16	35.03
1.04	7.18	153.3	12.90	<0.05	13.22	42.14
2.99	6.82	144.6	13.35	<0.05	13.68	69.38
5.08	6.75	122.8	13.34	<0.05	13.81	98.92

Sample ID	TOC (mg/L)	DOC (mg/L)	Turbidity-24 hr. (NTU's)
Initial (raw Pk-09 water)	<0.1	<0.1	0.86
0.13	<0.1	<0.1	0.51
0.52	<0.1	<0.1	0.48
1.04	<0.1	<0.1	0.47
2.99	<0.1	<0.1	0.41
5.08	<0.1	<0.1	0.20

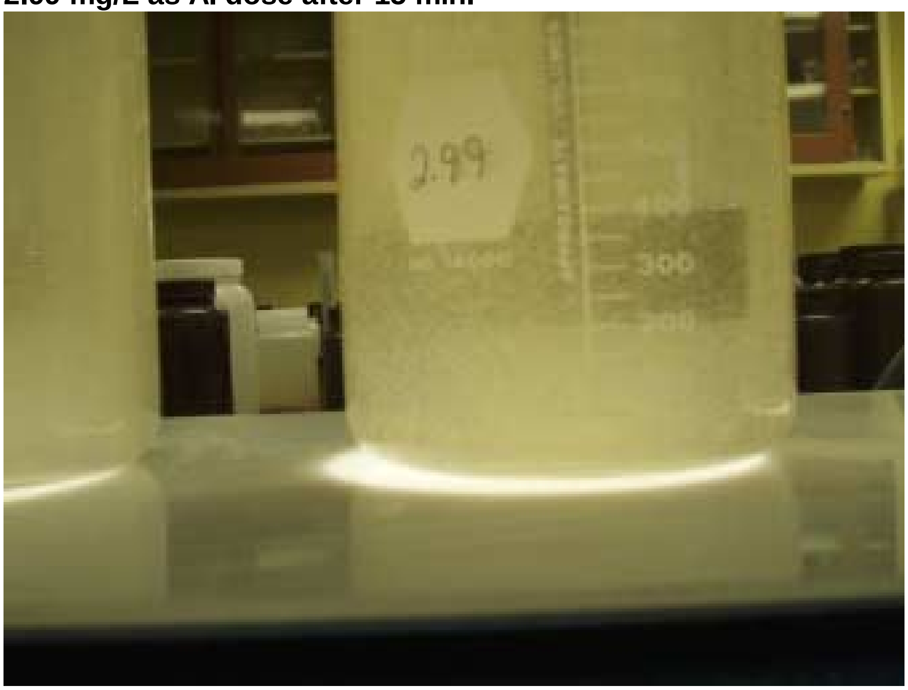
0.13mg/L Al dose after 15 min.

0.52 mg/L Al dose after 15 min.

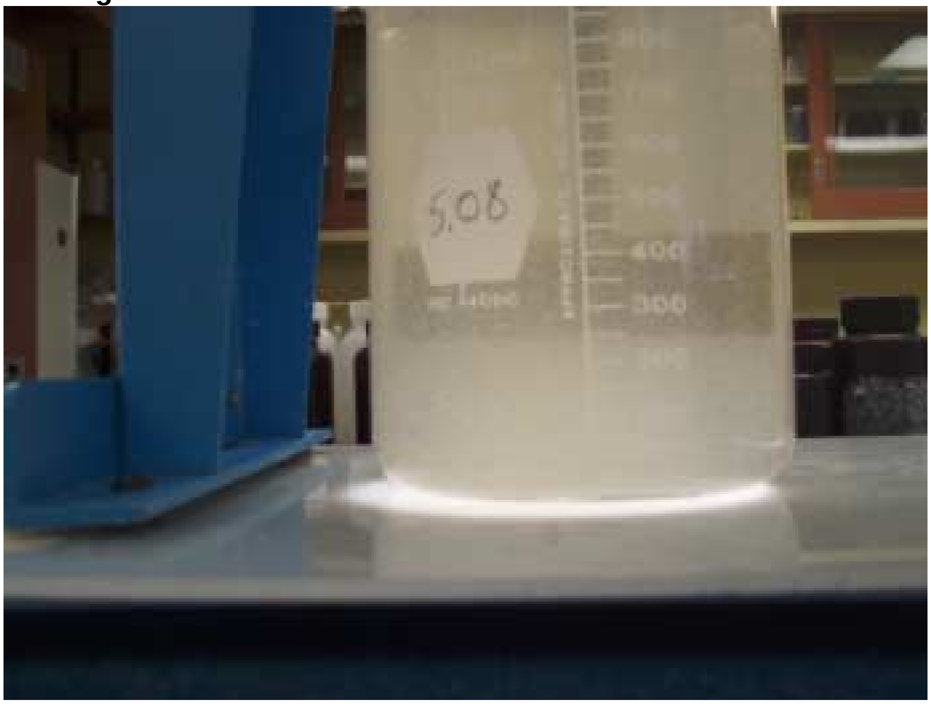
1.04 mg/L Al dose after 15 min.



2.99 mg/L as Al dose after 15 min.

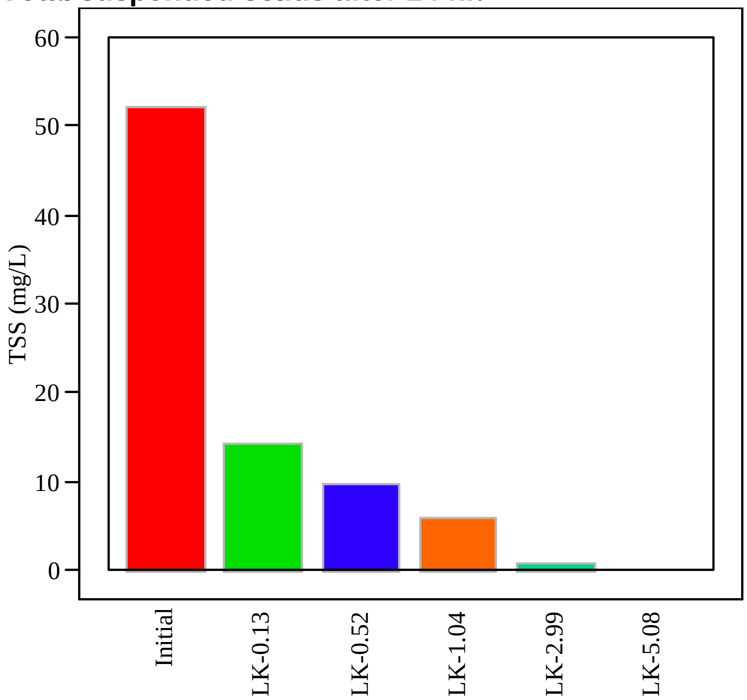


5.08 mg/L as Al dose after 15 min.

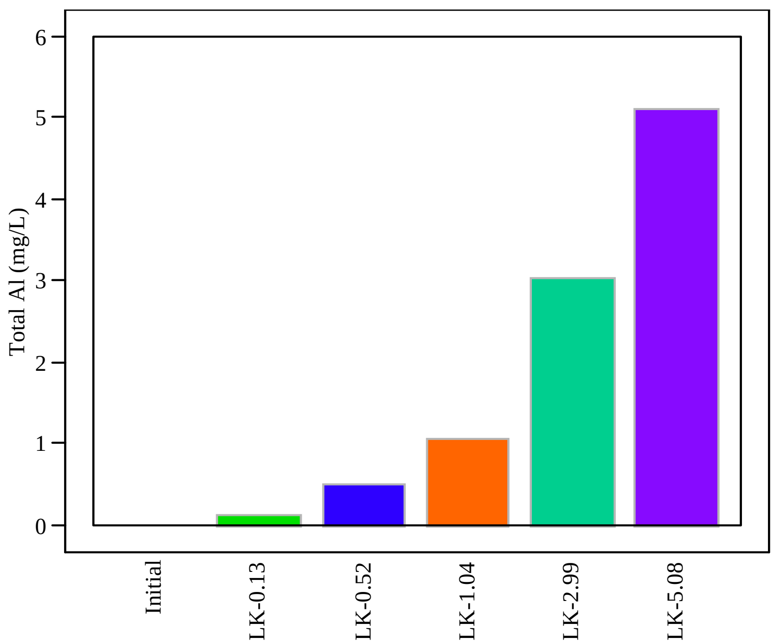


24 hour results after settling

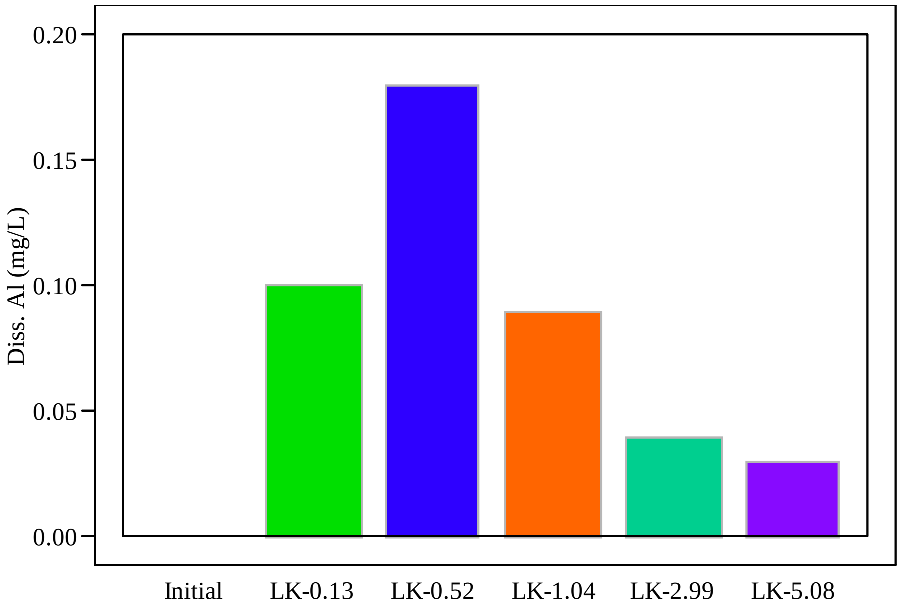
Total suspended solids after 24 hr.



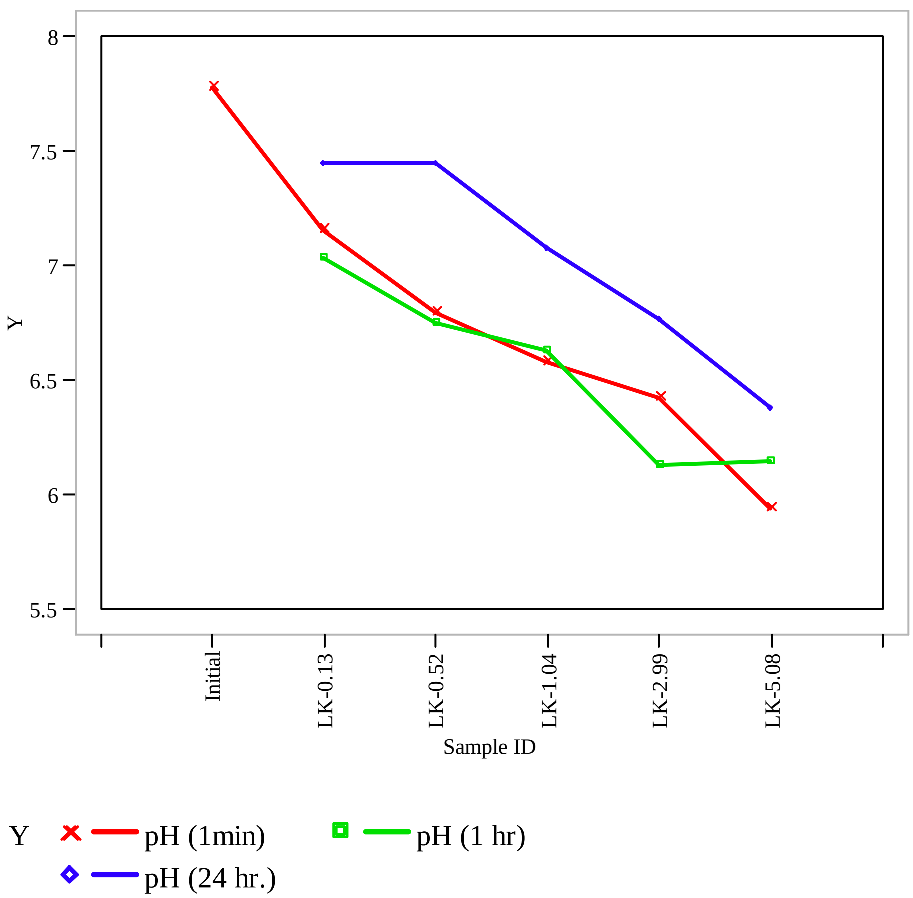
Total Al levels after 24 hr.



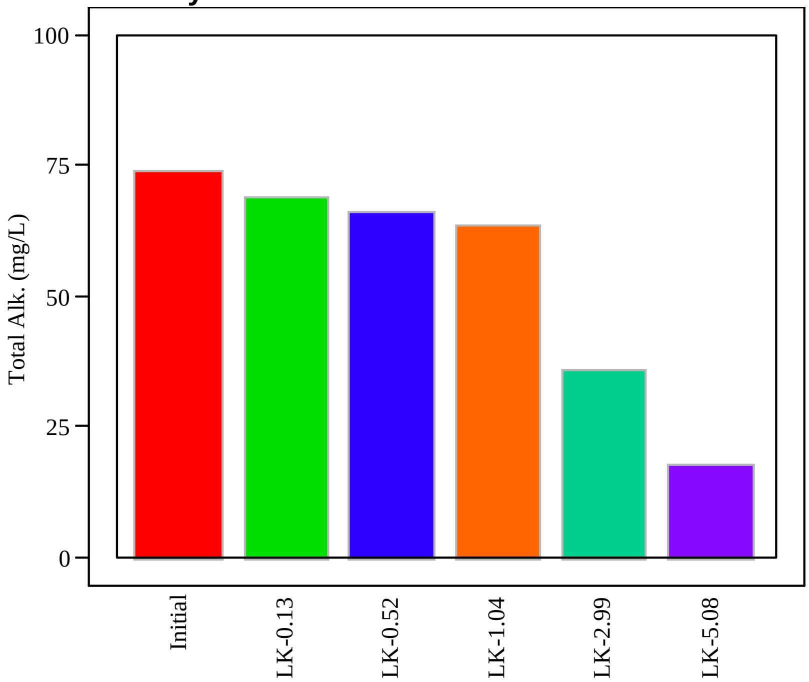
Dissolved Al levels after 24 hr.



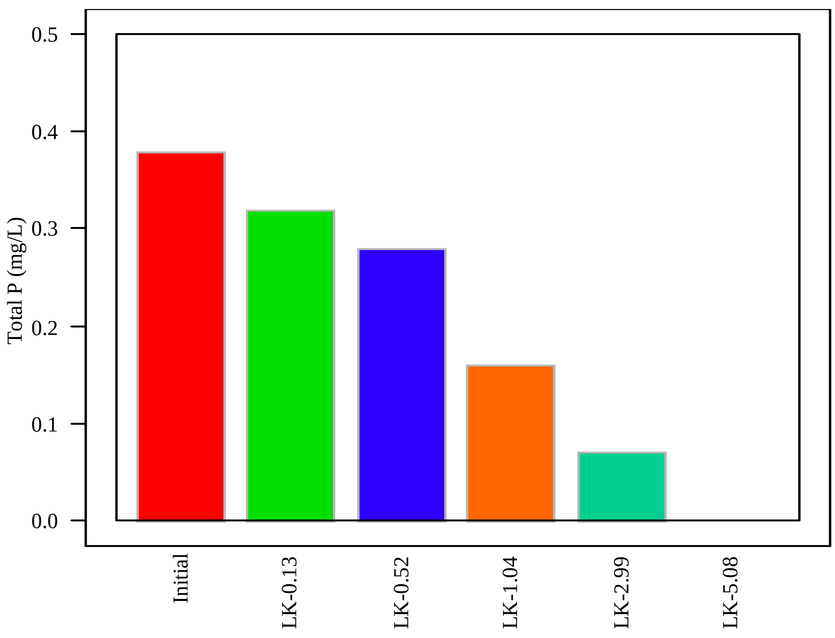
pH levels by dose and time



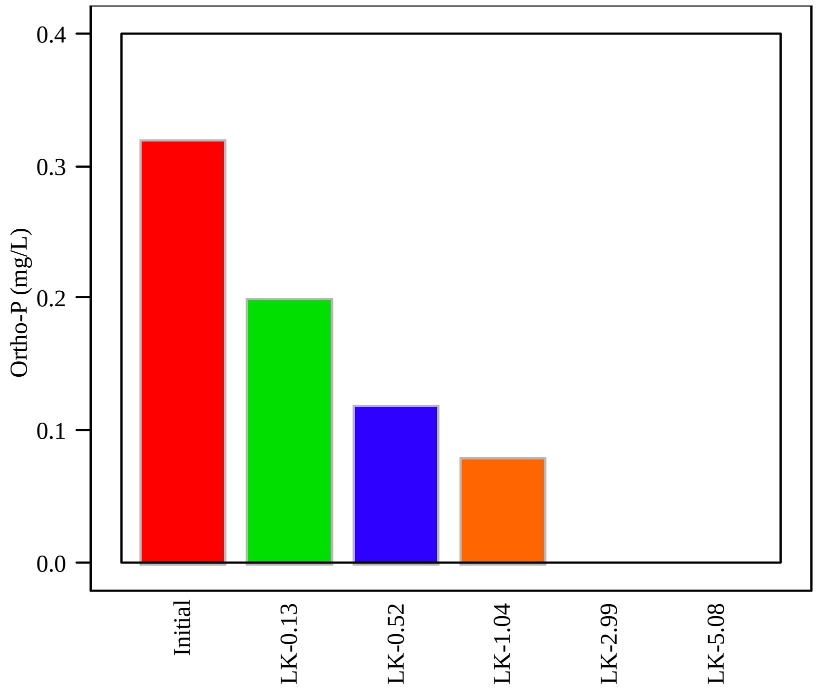
Total alkalinity after 24 hr.



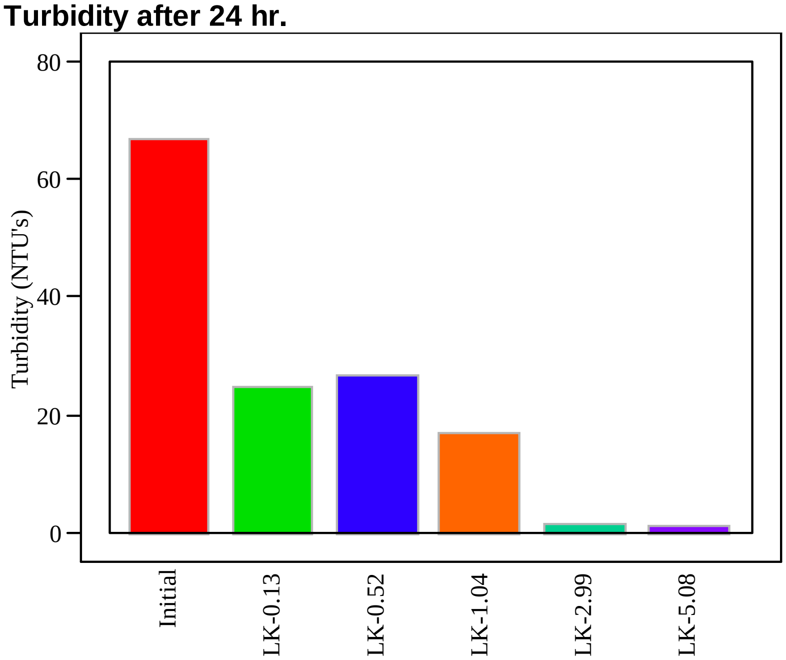
Total P after 24 hr.



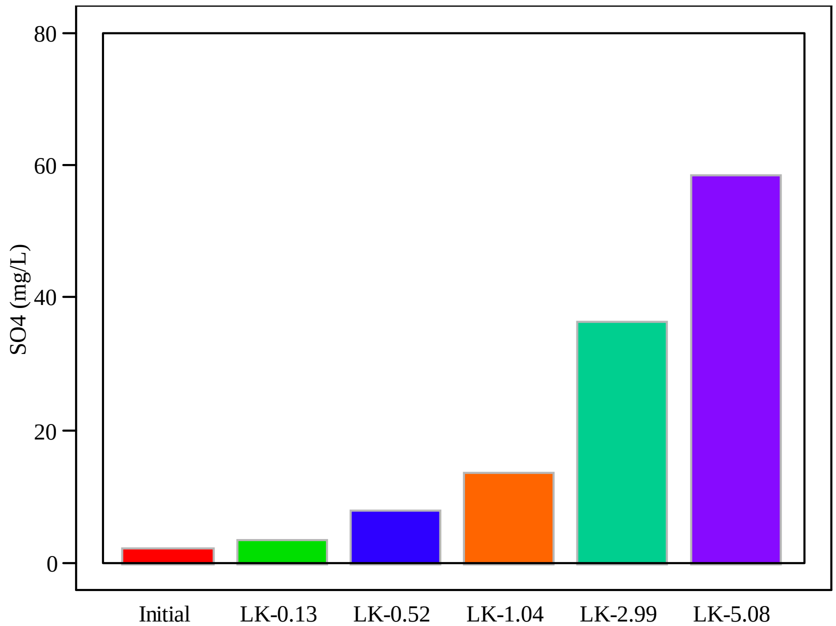
Ortho-P after 24 hr.



Turbidity after 24 hr.



Sulfate levels after 24 hr.



Acknowledgements

Thanks to Jeff Herr and Paul Jensen of PBS&J for providing invaluable information toward the completion of this report.

Literature Cited

Baker, J.P. and C.L. Schofield. 1982. Aluminum toxicity to fish in acidic waters. Water Air Soil Pollution 18: 289-309.

Cooke, G.D. and R.H. Kennedy. 1981. Precipitation and inactivation of phosphorous as a lake restoration technique. EPA-600/3-81-012.

Driscoll, C.T., J. Baker, J. Bisogni, and C. Schofield. 1980. Effects of aluminum speciation on fish in dilute, acidified waters. Nature (London) 284: 161-164.

Harper, H.H. 1990. Long Term Performance Evaluation of the Alum Stormwater Treatment System at Lake Ella, Florida. Final Report for Florida Department of Environmental Regulation, Project WM339.

Kane, D.A. and C.F. Rabeni. 1987. Water Resources 21: 663.

Lamb, D.S. and G.C. Bailey. 1981. Acute and chronic effects of alum to midge larvae (*Diptera; Chironomidas*). Bull. Environ. Contam. Toxicol. 27: 59-67.

Livingston, H.H. Harper, and J.L. Herr. 1994. The Use of Alum Injection to Treat Stormwater. Proceedings of the Second Annual Conference on Soil and Water Management for Urban Development-Creative Stormwater Management held in Sydney Australia, Sept. 6-7, 1994.

Narf, R.P. 1978. An Evaluation of Past Aluminum Sulfate Lake Treatments: Present Sediment Aluminum Concentrations and Benthic Insect Communities. Wiscosin Dept. Natural Resources, Madison, WI.

Woodward, D.F., A.M. Farag, M.E. Muller, E.E. Little, and F.A. Vertucci. 1989. Sensitivity of endemic Snake River cutthroat trout to acidity and elevated aluminum. Trans. Am. Fish. Soc. 118(6): 630-643.