

# Does Alum Addition Affect Benthic Communities and Metal and Nutrient Cycling? A Case Study from Grand Lake St. Marys, Ohio

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7. Nogaro Geraldine; AJ Burgin, Chad Hammerschmidt, 2012, Influence of alum addition on metal and nutrient cycling in Grand Lake Saint Marys, Ohio, In Environmental Science Graduate Programs spring seminar series, Ohio State University, April 6 2012, Columbus OH
8. Nogaro Geraldine, Chad Hammerschmidt, AJ Burgin, 2011, Alum influence on metal and nutrient cycling and benthic communities in a shallow eutrophic lake, In Annis water Resources Institute seminar series, Grand Valley State University, July 22 2011, Muskegon MI
9. Nogaro Geraldine; Chad Hammerschmidt, AJ Burgin, 2011, Influence of alum addition on metal and nutrient cycling in Grand Lake Saint Marys, Ohio, In North American Benthological Society

Does Alum Addition Affect Benthic Communities and Metal and Nutrient Cycling? A Case Study from Grand Lake St. Mary

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## Annual Report

# **Does Alum Addition Affect Benthic Communities and Metal and Nutrient Cycling? A Case Study from Grand Lake St. Marys, Ohio**

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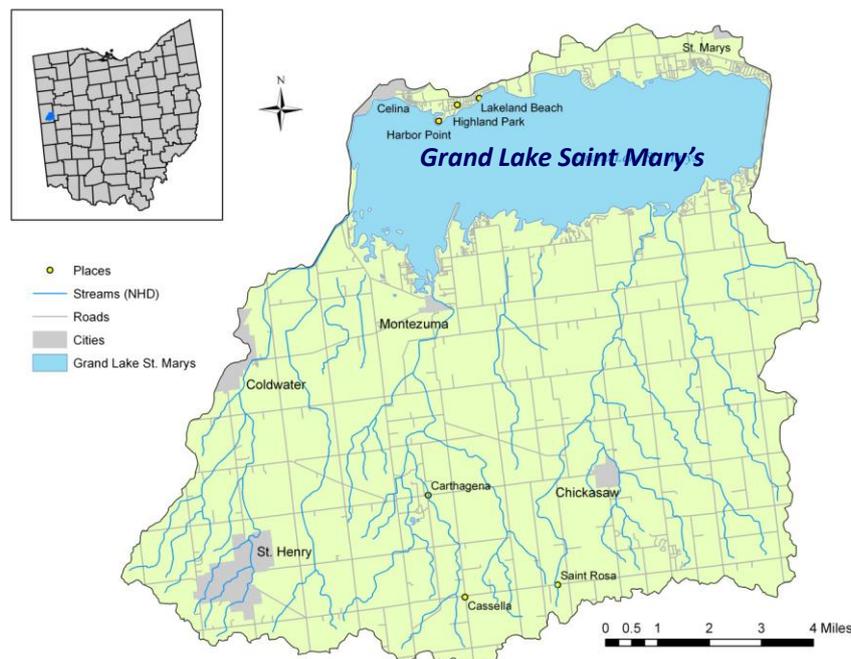
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### **1. SUMMARY**

Grand Lake Saint Mary's (GLSM) experiences severe eutrophication due to high loadings of phosphorus (P) and associated blooms of harmful cyanobacteria. The decline of the lake's water quality has caused a significant loss to the regional economy. The Ohio EPA experimentally added aluminum sulfate (alum) to GLSM to chemically treat P, which can reach 1,000 µg/L. Our study focuses on the ecological consequences of alum additions on benthic microbial and invertebrate communities, as well as associated nutrient and metal cycling in the lake. Our approach combines field sampling of non-alum amended sites and alum-amended sites on GLSM with a mesocosm experiment that manipulated bioturbating organisms and alum addition. Water and sediment samples from the field and mesocosm experiment were analyzed for physicochemical parameters, dissolved ions, dissolved and particulate metals, and microbial activities. Our results indicate that alum addition can greatly increase dissolved aluminum in surface and pore waters compared to the non-alum amended sites, likely beyond toxicity thresholds for some organisms. Alum treatment also increased sulfate in surface and pore waters. The increase of metals and alternative electron acceptors may feedback to alter microbial community dynamics and invertebrate communities. Our results showed that the presence of bioturbating fauna can reduce the effectiveness of alum addition by stimulating phosphate releases from the sediment to the water column. Results from this work will enhance our understanding of the ecological consequences of alum additions in GLSM and, in general, eutrophic freshwater ecosystems elsewhere.

## 2. PROBLEM AND RESEARCH OBJECTIVES

Excessive nutrient loadings to aquatic ecosystems cause eutrophication, a process associated with increased primary production and simplification of biodiversity (Smith et al., 1999). GLSM is Ohio's largest inland lake at 52.4 km<sup>2</sup>, with a maximum depth of about 2 m and a watershed of 230 km<sup>2</sup> (Fig. 1). Cultural eutrophication due to agriculture (cropland) and livestock operations in 90% of GLSM's watershed has resulted in excessive P loadings to the lake and subsequent blooms of toxic blue green algae (Hoorman et al., 2008). A lake classified as being eutrophic typically has between 25–50 µg total P L<sup>-1</sup>; surface water of GLSM has contained in excess of 1,000 µg L<sup>-1</sup> of P during the summer (Hoorman et al., 2008).



**Fig. 1** Grand lake Saint Mary's watershed

Eutrophication has ecological and economic consequences. Decomposition of the produced biomass results in depleted levels of dissolved oxygen, which can lead to fish kills such as those that occurred in GLSM on June 28 and 29, 2009 (Allen, 2009). Furthermore, blooms of such bacteria can release high levels of neuro- and hepatotoxins to the water, which led the Ohio Environmental Protection Agency (OH EPA) to declare a “no contact” rule for GLSM during the summers of 2009 and 2010: nine people became sick and three dogs died after contact with the lake (Barlow, 2010). Because GLSM is a popular recreation lake for boating, fishing, and swimming, the decline of the lake's water quality also has caused a significant economic loss to local businesses and the overall livelihood of the region (Barlow, 2010). Local home and business owners have pressured state leaders to find short-term solutions to reduce cyanobacteria blooms in GLSM. Management of eutrophication due to high P loadings is difficult because P, unlike nitrogen, does not have an atmospheric component, and is therefore retained completely in the system unless removed physically. Phosphorus can be removed from the lake only by discharge (water or sediment removal) or sorbing permanently to the sediments (Carpenter et al., 1999). Addition of aluminum sulfate (alum) to GLSM has been proposed by the OH EPA and the OH Department of Agriculture (DoA), together with the environmental consulting group TetraTech, as a short-term treatment to decrease P levels and combat the harmful algal blooms.

Alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ) can be used to chemically treat P-enriched eutrophic lakes. When added to water, alum hydrolyzes to form an amorphous floc of  $\text{Al}(\text{OH})_3(\text{s})$  ( $\text{p}K_{\text{sp}} = 32$ ) that has a high adsorption affinity for P (Huang et al., 2002) and can react with  $\text{PO}_4^{3-}$  to form insoluble  $\text{AlPO}_4(\text{s})$  ( $\text{p}K_{\text{sp}} = 21$ ). The primary goal of alum additions is to form an  $\text{Al}(\text{OH})_3(\text{s})$  floc on the sediment surface that minimizes P release to the water column. Although alum has been used to treat excess P in lakes worldwide since the 1970's, the solubility, chemistry, and toxicity dissolved Al after an alum treatment are still not well known (Kennedy and Cooke, 1982; Gensemer and Playle, 1999). Water pH plays a key role in Al chemical phases after an alum treatment because  $\text{Al}(\text{OH})_4^-$  dominates at high pH,  $\text{Al}(\text{OH})_3$  between 6 and 8 and free  $\text{Al}^{3+}$  at low pH (Kennedy and Cooke, 1982). Berkowitz et al. (2005) showed in a laboratory study that alum addition to water samples resulted in a rapid initial pH decrease followed by a gradual recovery and an increase of dissolved Al concentrations up to  $2500 \mu\text{g L}^{-1}$  after 17 days and then a decrease to  $< 250 \mu\text{g L}^{-1}$  after 150 days. Importantly, and after treatment with alum, there was a 35-d period in Lake Elsinore when aluminum exceeded  $1000 \mu\text{g L}^{-1}$  at a pH of about 8.5 (Berkowitz et al., 2005)—conditions that can cause short-term toxicity (Gensemer and Playle, 1999). Another consequence of alum additions is an increased amount of sulfate ( $\text{SO}_4^{2-}$ ) in the system. Sulfate is a desirable alternative electron acceptor for anaerobic microbial metabolism, and increasing  $\text{SO}_4^{2-}$  has been associated with increased  $\text{SO}_4^{2-}$  reduction rates (Vile et al., 2003; Weston et al., 2006).  $\text{SO}_4^{2-}$  reduction results in sulfide ( $\text{S}^{2-}$ ), which is toxic to benthic organisms and interferes with many sensitive biomolecules, including enzymes (Wang and Chapman, 1999).

This study focuses on the ecological consequences of alum additions on benthic microbial and invertebrate communities, as well as associated nutrient and metal cycling. We ask the *overarching question: **How does the addition of alum affect invertebrate bioturbation, microbial nutrient processing and metal cycling in Ohio's GLSM?***

From this overarching question, we have tested three specific hypotheses ( $H_1$ – $H_3$ ) with an approach that combined field sampling of the already extant alum addition sites on GLSM with a mesocosm experiment that manipulated bioturbating organisms and alum addition levels.

*H<sub>1</sub>: Alum additions increase Al concentrations in the water and near-surface sediments of GLSM.*

*H<sub>2</sub>: Alum additions increase sulfate levels in GLSM, which in turn will enhance microbial sulfate reduction rates and generation of sulfide.*

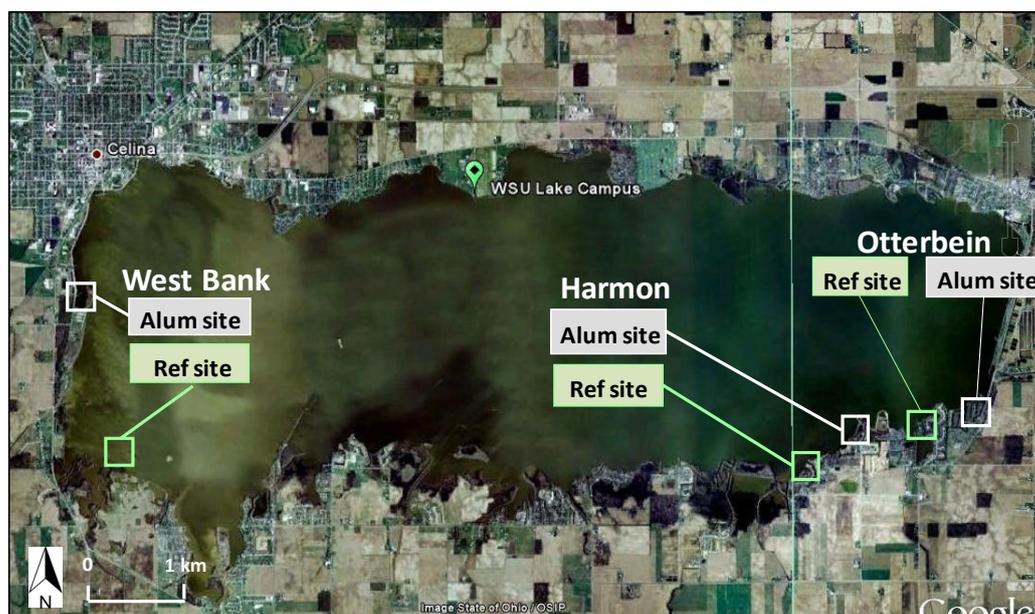
*H<sub>3</sub>: Alum additions will decrease microbial activity and invertebrate bioturbation in the sediment, which, in turn, will affect nutrient and metal cycling of GLSM.*

### 3. FIELD SAMPLING IN NOVEMBER 2010

#### 3.1. Methodology

In September 2010, the OH EPA conducted a pilot study to examine the efficacy of alum additions on planktonic growth in three small bays of GLSM: Harmon's Channel, Otterbein Channel No.1 and West Bank Marina. We used these alum test locations, with matched reference sites, to investigate the effects of alum treatment on metal and nutrient cycling in surface waters and lake sediments (Fig. 2). The dosage of alum was 31.6 mg/L as alum and sodium aluminate (used as a buffer), which was applied on September 20, 2010 in the three shallow bays of GLSM (Table 2). The total cost of such alum treatment was \$61,500 (TetraTech, 2010).

In November 11, 2010 (i.e., about 3 weeks after the alum addition by the OH EPA), we performed *in situ* measurements and sampling of water and sediment at the alum-amended sites and matched reference sites (i.e., with no alum addition) of Harmon, Otterbein and West Bank Marina locations of GLSM (Fig. 2). We worked in collaboration with Dr. Robert Hiskey, Associate Professor of Biological Sciences at Wright State University – Lake Campus. Dr. Hiskey has offered his boat and equipment at the Lake Campus marina to collect water and sediment samples on GLSM. Surface water and sediments from three alum treatment and reference sites were analyzed for physicochemical parameters, dissolved ions, dissolved and particulate metals, and microbial activities. We expected that alum additions would increase Al concentrations in the water and near-surface sediments of GLSM. We also expected that alum additions would increase sulfate levels in GLSM, which in turn will enhance microbial sulfate reduction rates and generation of sulfide.



**Fig. 2.** Map of the aluminum sulfate addition (alum) and reference (ref) sites of Harmon, Otterbein and West Bank Marina locations in Ohio's Grand Lake Saint Mary's.

**Table 1.** Characteristics of the three demonstration project locations (TetraTech, 2010)

Site	Area (m <sup>2</sup> )	Dosage (kg Al)	Depth (m)
Harmon	53,000	2,012	1.2
Otterbein	31,000	1,449	1.5
West Bank	36,000	2,083	2.0

At each site, surface water samples were analyzed for dissolved oxygen, pH, temperature, specific conductance, chlorophyll, redox potential, turbidity, total suspended solids (TSS), dissolved and particulate inorganic and total phosphorus, dissolved nitrate, nitrite, ammonium, dissolved sulfate, and organic carbon with standard methods (APHA et al., 1995). We also measured dissolved and particulate aluminum and other biologically active metals that may be affected by alum addition, including copper, nickel, zinc, cobalt, lead, manganese, and iron. Intact, undisturbed sediment cores were collected and sectioned into 0–1, 1–2, 2–3, and 3–4 cm depth horizons and pore water extracted by vacuum filtration (Hammerschmidt et al., 2004). Filtered water also was measured for metals, sulfide, phosphate, nitrate, nitrite, ammonium, and organic carbon. Water and sediment was sampled with trace-metal clean techniques (Gill and Fitzgerald, 1987) and transported promptly to Wright State University for processing and analysis. Sediments also were sampled to quantify microbial activities (hydrolytic and dehydrogenase) as well as invertebrate density and species richness. Hydrolytic and dehydrogenase activities indicate aerobic enzymatic and respiratory microbial activities, respectively.

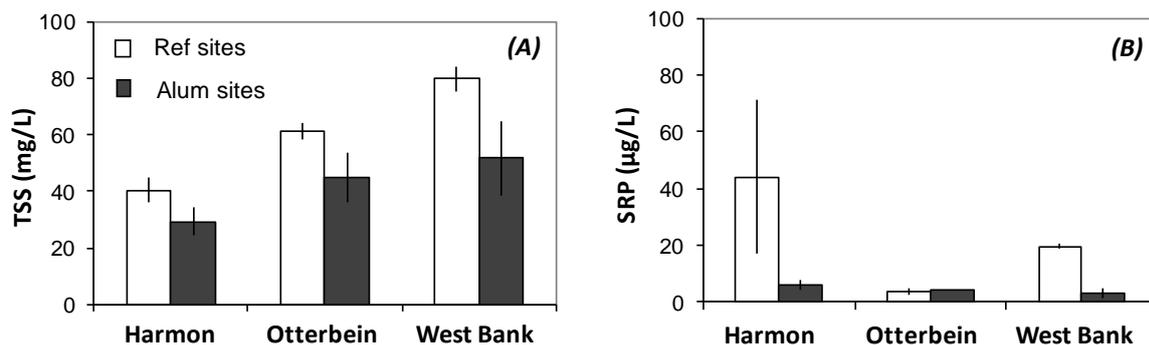
### 3.2. Principal findings

Our results indicate that alum-treated locations experienced an increase of pH and a decrease of turbidity, chlorophyll and redox potential in the surface water compared to the reference sites (Table 2). The increase of pH can be attributed to a buffer (i.e., sodium aluminate) added with the acidic alum, whereas reductions of turbidity, chlorophyll, and redox potential are consistent with reduced primary production.

**Table 2.** *In-situ* measurements in the surface water of the reference (i.e., Ref) and the alum-treated (i.e., Alum) sites of Grand Lake Saint Mary’s in November 11, 2010

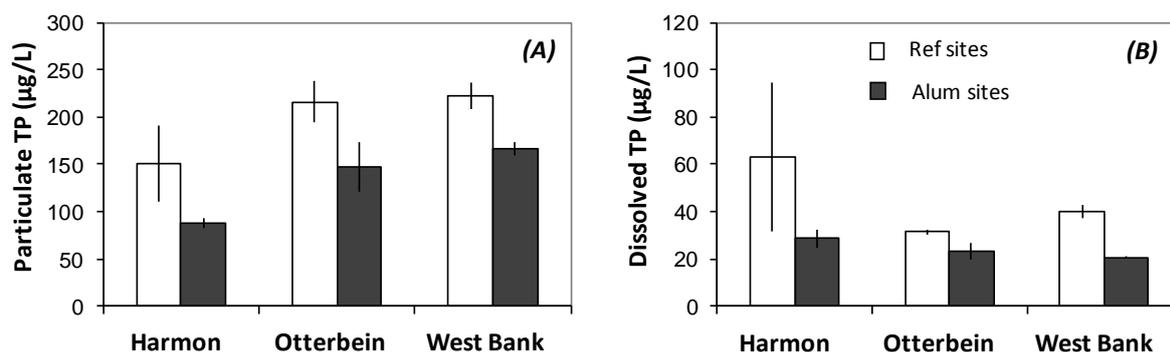
	Harmon		Otterbein		West Bank	
	Ref	Alum	Ref	Alum	Ref	Alum
<b>pH</b>	7.98	8.22	8.17	8.81	8.84	9.79
<b>Turbidity (NTU)</b>	43.5	26.5	48.7	26.0	8.5	7.9
<b>Chlorophyll (ug/L)</b>	11.7	5.9	14.1	6.7	11.7	5.9
<b>Redox potential (mV)</b>	223	210	249	158	217	160

As expected, alum additions decreased total suspended solids (TSS) concentrations in surface water (Fig. 3A). Soluble reactive phosphorus (SRP) also was reduced substantially at two of the three test locations (Fig. 3B). SRP concentrations were relatively low (7–40  $\mu\text{L}^{-1}$ ) because it is the most available form of P for biological uptake and the sampling was performed in November (i.e., end of algae growing season) in small embayments.



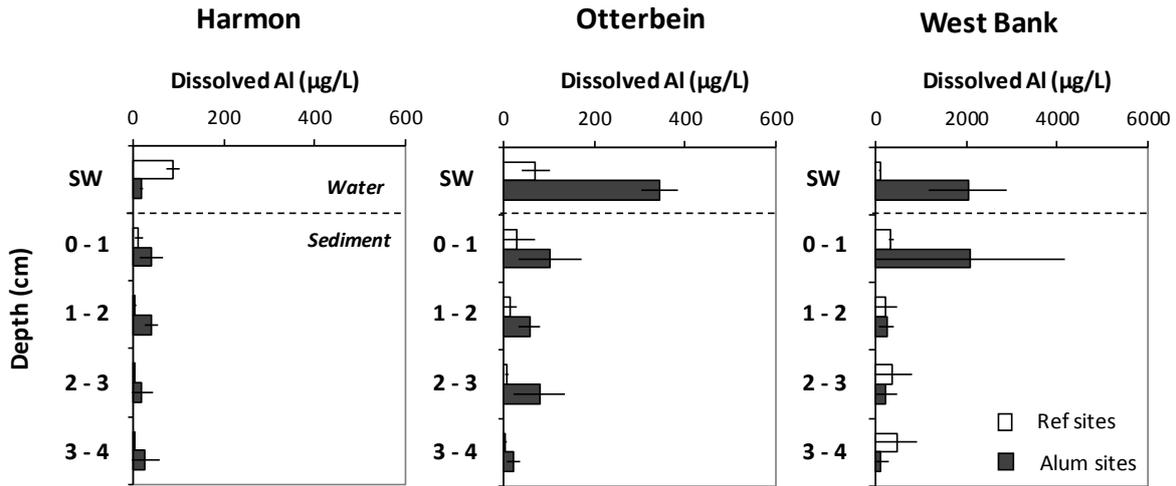
**Fig. 3.** Concentrations of (A) total suspended solids (TSS) and (B) soluble reactive phosphorus (SRP) in the surface water of the reference (ref) and alum-amended (alum) sites of Harmon, Otterbein and West Bank Marina locations in GLSM (mean  $\pm$  1 SE,  $n=3$ ).

Moreover, the alum treatment decreased the dissolved total P (Fig. 4A) and particulate total P (Fig. 4B) in comparison with the reference sites. However, and even after the treatment, the lake surface water was still highly eutrophic because concentration of dissolved + particulate TP remained greater than 100  $\mu\text{g/L}$  in each of the three bays (Fig. 4).



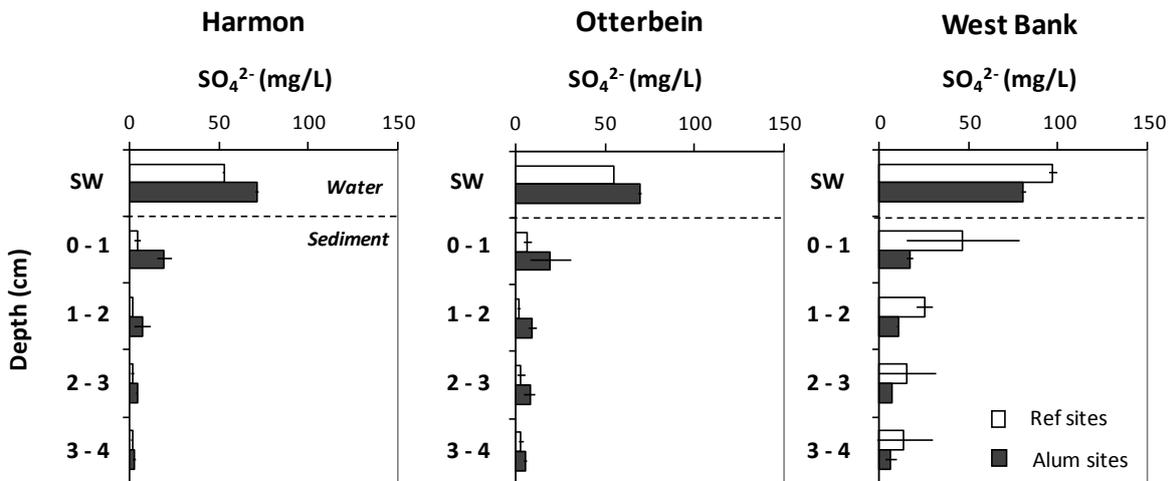
**Fig. 4.** Concentrations of (A) dissolved total phosphorus (dissolved TP) and (B) particulate total phosphorus (particulate TP) in the surface water of the reference (ref) and alum-amended (alum) sites of Harmon, Otterbein and West Bank Marina locations in GLSM (mean  $\pm$  1 SE,  $n=3$ ).

A primary concern with alum additions is potential and unintentional toxicological effects of aluminum (Al) on biotic communities. Al has relatively simple chemical speciation in water, existing principally as free  $\text{Al}^{3+}$  at  $\text{pH} < 5$ , insoluble  $\text{Al}(\text{OH})_3(\text{s})$  and  $\text{Al}(\text{OH})_3^0$  at  $\text{pH}$  between about 5 and 9, and dissolved  $\text{Al}(\text{OH})_4^-$  at  $\text{pH} > \sim 9$ . Hence, differences and changes in  $\text{pH}$  can affect the solubility and speciation of Al. Our preliminary results indicate high levels of Al in filtered ( $0.45 \mu\text{m}$ ) surface and pore waters of Otterbein and West Bank alum test locations compared to the reference sites (Fig. 5)—mean levels of Al in filtered surface water were  $340$  and  $2030 \mu\text{g L}^{-1}$ , respectively. These levels are orders of magnitude greater than those predicted from solubility product estimates of  $\text{AlPO}_4$  and  $\text{Al}(\text{OH})_3(\text{s})$  at  $\text{pH}$  7–10, which suggests that either natural organic ligands may promote dissolution of the Al minerals or that a substantial fraction of the Al is associated with colloids. Such levels of Al are associated commonly with toxicity to many species of phytoplankton, macrophyte, aquatic invertebrate and fish (Gensemer and Playle, 1999).



**Fig. 5.** Aluminum (Al) concentrations in filtered surface and pore waters of the reference (ref) and alum-amended (alum) sites of Harmon, Otterbein and West Bank Marina locations in GLSM (mean  $\pm$  1 SE,  $n=3$ ). Note the difference in x-axis scale between the West Bank site and the Otterbein and Harmon sites.

The ecological effects of alum additions are not well known, although this chemical treatment has been used in eutrophic lakes worldwide for four decades (Kennedy and Cooke, 1982). In particular, the effects of alum treatment on benthic microbial and invertebrate communities remain poorly understood. Our results showed decreased total P, TSS, and chlorophyll in the alum test sites (Table 2, Figs. 3 & 4); however, the pH of surface water was increased greatly in each of the alum test sites compared to reference sites (Table 2). While the toxicity of dissolved Al to benthic invertebrates has been well studied under acidic to circumneutral conditions, little information is known about the effects of Al on invertebrates in alkaline water (Gensemer and Playle, 1999). Another consequence of alum additions is an increased amount of sulfate ( $\text{SO}_4^{2-}$ ) in the system. Increased levels of sulfate were measured in the surface water and pore waters of the alum test sites at Harmon and Otterbein (Fig. 6). Sulfate is used as alternative electron acceptor by anaerobic microbial communities and converted into sulfide ( $\text{S}^{2-}$ ), which can be highly toxic to benthic organisms.



**Fig. 6.** Concentrations of sulfate ( $\text{SO}_4^{2-}$ ) in the pore water of the reference (ref) and alum test sites of Harmon, Otterbein and West Bank Marina (mean  $\pm$  1 SE,  $n=3$ ).

## 4. Field sampling in Spring/Summer 2011

### 4.1. Methodology

Our original experimental plan was to sample the untreated reference and alum test sites at each of three locations in the lake in spring and summer 2011. However, in May 2011, the OH EPA decided to treat the *main lake* with alum in order to remove P from the water column and avoid toxic algae bloom during the summer 2011. In June 2011, a high dose of alum was added to 16.2 km<sup>2</sup> (~30% of total lake area) of the central part of GLSM (Figs. 7 and 8). The alum dose was applied from June 2<sup>nd</sup> to June 29<sup>th</sup> and corresponded to 390,700 kg Al from alum and 497,265 kg Al from sodium aluminate (OH EPA, 2011).



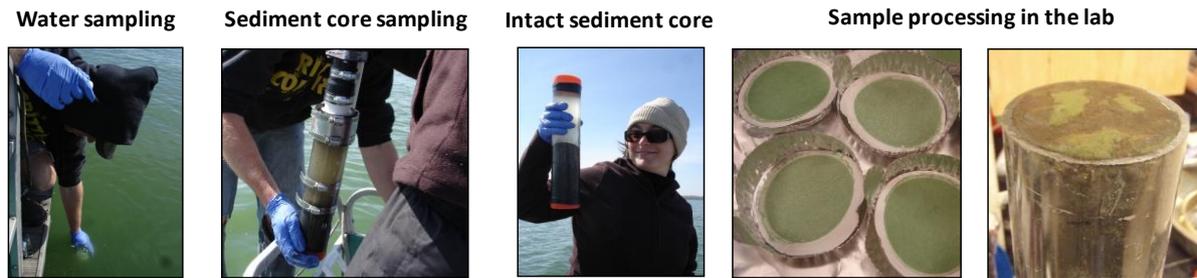
**Fig. 7.** Pictures of GLSM and the boat applying alum in June 2011 in the central area of the lake.

In spring and summer 2011, we measured biogeochemical characteristics of water and sediment at five sites of GLSM before (June 2<sup>nd</sup> 2011) and after (June 29<sup>th</sup> 2011) the alum addition (Fig. 8). At each site, we measured physicochemical parameters, dissolved ions, TSS, dissolved and particulate metals, and microbial activities in three replicate water samples and sediment cores (Fig. 9). Three replicates of benthic samples also were collected before and after alum addition to measure invertebrate density and species richness.



**Fig. 8.** Map of the sampling sites and area of alum addition applied in June 2011 to the central area of Grand Lake Saint Mary's.

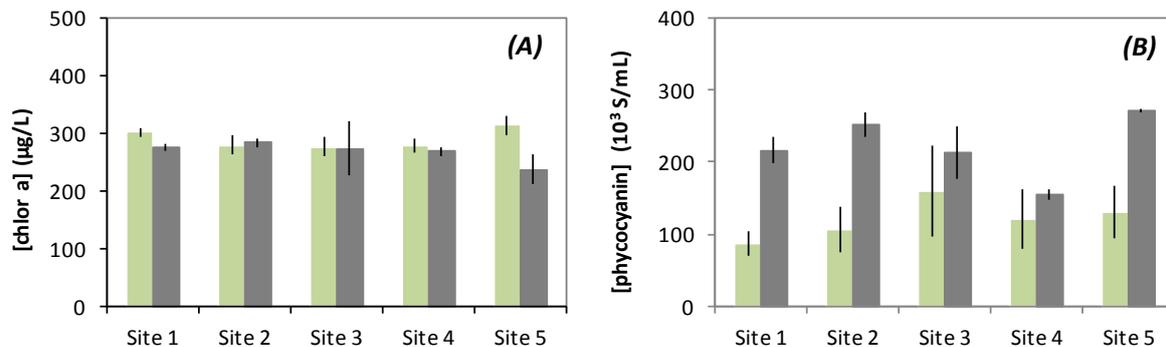
For each field expedition (before and after alum addition), metal analyses were performed on 30 filtered (i.e., 3 replicates, 5 sites, 2 dates) and 30 samples of filtered particles from surface water. We also measured 120 sediment samples (i.e., 3 replicates, 5 sites, 4 depths, 2 dates) and 120 pore water samples resulting in a total of 300 samples for metal analyses. We also measured 90 water samples (i.e., 3 measurements, 3 replicates, 5 sites, 2 dates) for dissolved gases, 30 surface water and 120 pore water samples for nutrients and dissolved organic carbon (DOC), 30 samples for TSS, 240 sediment samples (i.e., 3 replicates, 5 sites, 2 dates, 4 depths, 2 activities) for microbial activity and 30 sediment samples for invertebrate analyses.



**Fig. 9.** Pictures of water and sediment sampling and sample processing in the lab in June 2011.

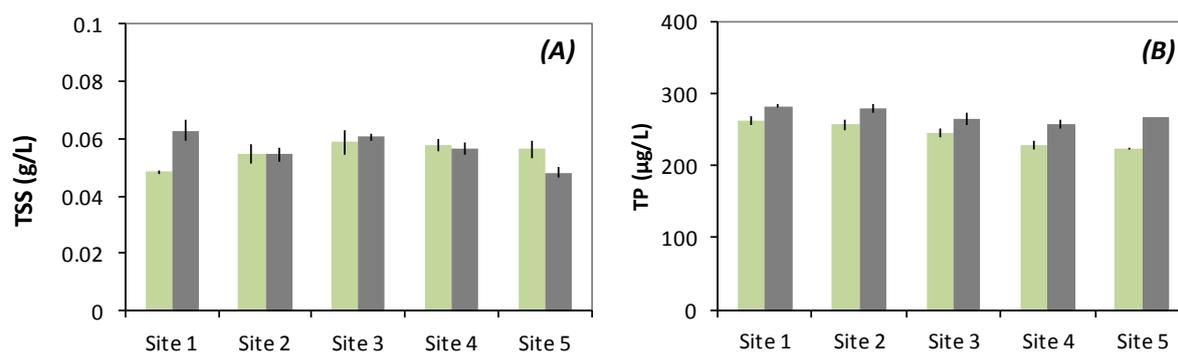
#### 4.2. Principal Findings

The alum addition on the main lake did not affect the chlorophyll concentrations in most of the sampling sites; only a small decrease in chlorophyll was measured at Site 5 after the alum addition in comparison with the pre-alum date (Fig. 10A). The phycocyanin content (i.e., cyanobacteria pigment) of the surface water increased at Sites 1, 2 and 3 of GLSM after the alum addition. These findings suggest that the alum addition did not limit growth of cyanobacteria in the lake, at least within the first week after alum application.



**Fig. 10.** Concentrations of (A) chlorophyll a and (B) phycocyanin (i.e., cyanobacteria pigment) in the surface water of the five sampling sites of GLSM (i.e., S1 to S5 from the west side to the east side of the lake) before (2<sup>nd</sup> June 2011) and after (29<sup>th</sup> June 2011) the alum addition (mean  $\pm$  1 SE,  $n=3$ ).

From our pre- and post-alum sampling of lake water, we observed that concentrations of TSS in GLSM were largely unchanged by the addition of alum (Fig. 11A). Compared to pre-alum levels, TSS was increased at Site 1, decreased at Site 5, and unchanged at the other three locations. In contrast, total P concentrations were increased slightly at all sites after the alum addition (Fig. 9B), suggesting that the alum treatment did not significantly remove P from the water column within the first few weeks after application. This is consistent with the observed increase of phycocyanin (i.e., cyanobacterial growth) throughout the month of June (Fig. 10B).



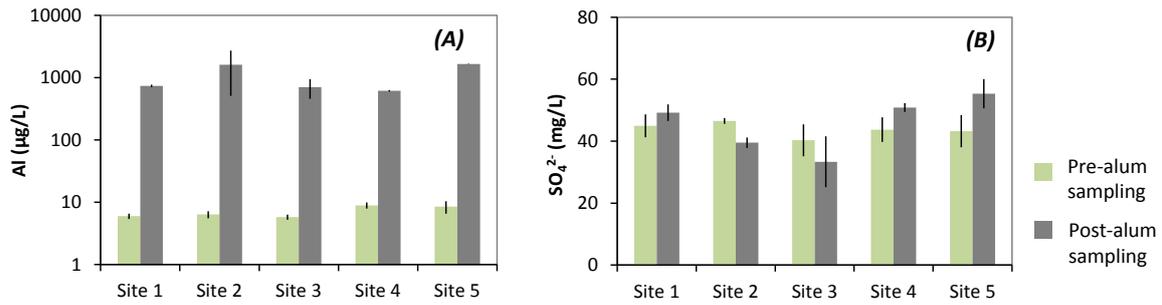
**Fig. 11.** Concentrations of (A) total suspended solids (TSS) and (B) total phosphorus (TP) in the surface water of the five sampling sites of GLSM before (2<sup>nd</sup> June 2011) and after (29<sup>th</sup> June 2011) the alum addition (mean  $\pm$  1 SE,  $n=3$ ).

The pH of lake water increased at each of the five sampling sites compared to before the alum addition (Table 3). Such a pH increase is caused by the dissolution of sodium aluminate buffer that is added with the alum. Indeed, levels of Al in filtered surface water after the alum addition (i.e., 614-1650  $\mu\text{g/L}$ ) were greatly increased compared to concentrations measured before the alum addition (i.e., 5.8-8.9  $\mu\text{g/L}$ , see on Fig. 12 A). Our first hypothesis that the alum additions would increase Al concentrations in the water and near-surface sediments of GLSM is strongly supported by these results. In a laboratory study, Berkowitz et al. (2005) found that alum addition to water resulted in a rapid initial pH decrease followed by a gradual recovery and an increase of dissolved Al concentrations up to 2500  $\mu\text{g L}^{-1}$  after 17 days and then a decrease to  $< 250 \mu\text{g L}^{-1}$  after 150 days. Importantly, and after treatment with alum, there was a 35-d period in Lake Elsinore when aluminum exceeded 1000  $\mu\text{g L}^{-1}$  at a pH of about 8.5 (Berkowitz et al., 2005)—conditions that can cause short-term toxicity (Gensemer and Playle, 1999). We observed similar pH and Al conditions in GLSM (Figs. 5 and 12A for the pilot alum study and the main lake alum addition, respectively). Berkowitz and colleagues (2005) also found that  $\text{Al}(\text{OH})_3(\text{s})$  formed after alum treatment undergoes geochemical transformations that may decrease its sorption capacity for P and reduce the effectiveness of the alum treatment.

Sulfate concentrations in the surface water did not differ significantly before and after the alum treatment (Fig. 12B), which did not support our second hypothesis stating that alum additions would increase sulfate levels in GLSM. The absence of an increase of sulfate concomitant with Al suggests that sulfate was removed more efficiently from the water column, possibly by either physical (e.g., precipitation) or biological processes (e.g., reduction, uptake).

**Table 3.** *In-situ* pH measurements in the surface water of the five sampling sites of GLSM before (2<sup>nd</sup> June 2011) and after (29<sup>th</sup> June 2011) the alum addition (mean  $\pm$  1 SE,  $n=3$ ).

pH surface water	Site 1	Site 2	Site 3	Site 4	Site 5
Before alum	8.6 $\pm$ 0.0	8.7 $\pm$ 0.0	8.9 $\pm$ 0.1	8.8 $\pm$ 0.1	8.6 $\pm$ 0.0
After alum	9.1 $\pm$ 0.4	9.6 $\pm$ 0.0	9.5 $\pm$ 0.0	9.6 $\pm$ 0.0	9.4 $\pm$ 0.3

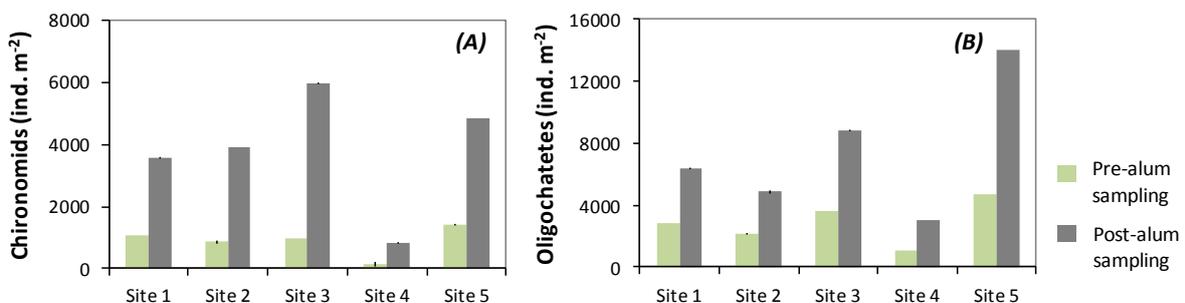


**Fig. 12.** Concentrations of (A) dissolved sulfate ( $\text{SO}_4^{2-}$ ) and (B) dissolved aluminum (Al) in the surface water of the five sampling sites of GLSM before (2<sup>nd</sup> June 2011) and after (29<sup>th</sup> June 2011) the alum addition (mean  $\pm$  1 SE,  $n=3$ ). Please note the Al concentration is on a logarithmic scale.

Few studies have focused on the ecological consequences of alum additions on benthic microbial and invertebrate communities. We conducted an invertebrate survey before (i.e., May 5<sup>th</sup> 2011) and after (July 14<sup>th</sup> 2011) the addition of alum to GLSM (Fig. 13). Our survey showed that the main taxa found in GLSM sediments were chironomid larvae and oligochaete worms, which are known to be the main taxa tolerant to eutrophic environments. Our results also showed an increase of invertebrate abundances between May and July, which was probably due to a seasonal growth effect and does not allow us to conclude any potential effect of alum on invertebrate abundance. Benthic invertebrate responses to alum addition have contrasting results. Steinman and Ogdahl (2008) observed that alum addition to a lake in Michigan resulted in a substantial reduction of invertebrate density. Moreover, Smeltzer et al. (1999) observed a decrease of invertebrate species density and richness during the first year after alum addition followed by a recovery two years later. In contrast, Narf (1990) observed a general increase of invertebrate density in five Wisconsin lakes after alum treatment. Such contrasted results may depend on the lake nutrient enrichment and geochemistry, the loadings of alum, and the composition of invertebrate communities.



**Fig. 13.** Pictures of the sediment sampling for the invertebrate survey performed before (5<sup>th</sup> May 2011) and after (14<sup>th</sup> July 2011) alum addition

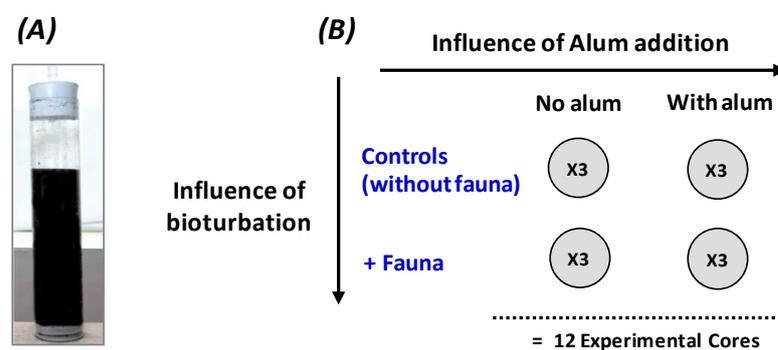


**Fig. 14.** Chironomid and oligochaetes counts from the invertebrate survey performed before (5<sup>th</sup> May 2011) and after (14<sup>th</sup> July 2011) alum addition (mean  $\pm$  1 SE,  $n=3$ )

## 5. LABORATORY MESOCOSM EXPERIMENT

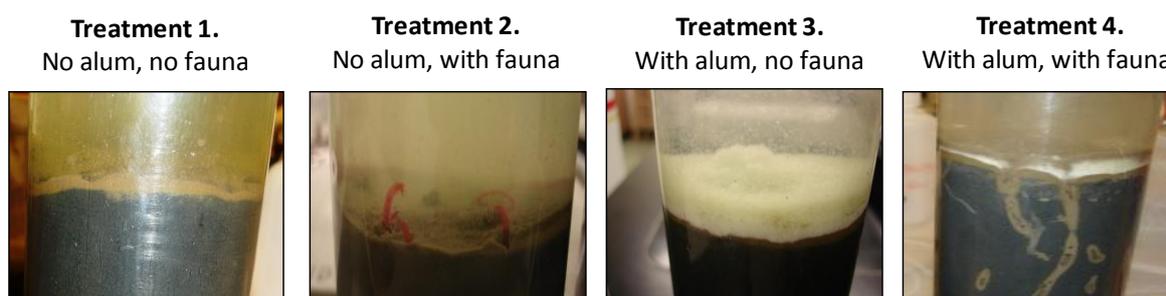
### 5.1. Methodology

Our laboratory mesocosm experiment used sediment cores (30 cm height, 7 cm inner diameter) collected from GLSM just prior to the experiment (Fig. 15A). The cores were filled with 10 cm of sediment overlain with 15 cm of water. Sediment was collected from GLSM in June 2011 in a non-alum-amended location and pre-screened with a 1-mm mesh sieve to ensure a relatively homogenous grain size and remove native macrofauna. Experimental cores were filled with aerated surface water from GLSM. With this design we were able to control the addition of alum and the density of macrofauna in order to test the influence and interaction of the two factors on nutrient and metal cycles at the water-sediment interface (Fig. 11B). The experimental cores readily permit (1) periodic sampling of overlying water for metal and chemical analyses, and 2) sectioning of sediment strata at the end of the experiment.



**Fig. 15.** (A) Picture of one experimental core and (B) design of the mesocosm experiment.

Invertebrates (chironomid larvae) were introduced to the cores after sediment installation. Species identity (i.e., *Chironomus plumosus*) and density (1,200 individuals  $m^{-2}$ ) of invertebrates for the fauna treatment were determined from the field survey samplings (i.e., Fig. 14A before alum addition). Invertebrates collected from GLSM and were introduced to some of the cores whereas other cores did not have animals and served as controls. Three replicate cores were used for each treatment: (1) no alum, no fauna; (2) no alum, with fauna; (3) with alum, with fauna; and (4) with alum and with fauna (Figs. 15B & 16).



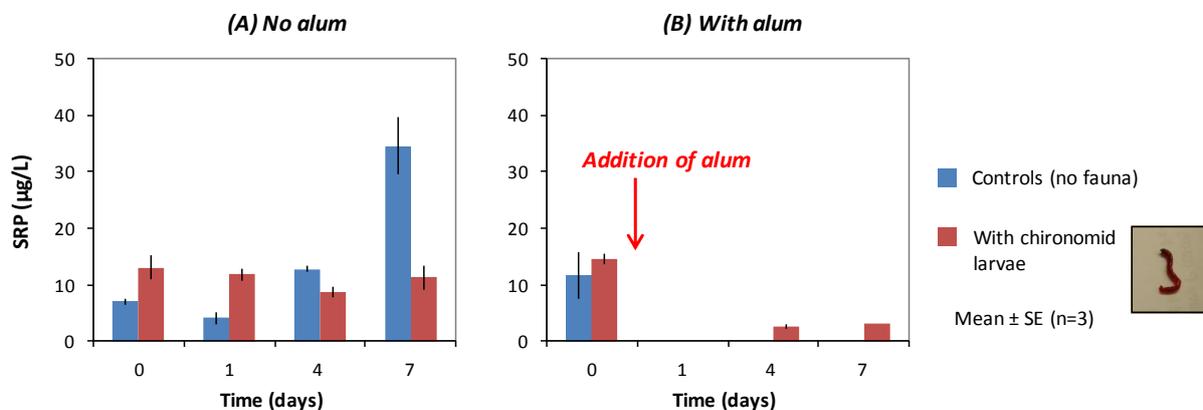
**Fig. 16.** Picture of different treatments of the experimental cores: (treatment 1) No alum, no fauna; (treatment 2) No alum addition, in presence of chironomid larvae; (treatment 2) with alum addition, absence of chironomid larvae; and (C) with alum addition, in presence of chironomid larvae.

The experiment was initiated by adding alum to the treatment mesocosms three days after the addition of fauna. Liquid alum was added in the designated experimental cores resulting in a total addition of 44 g Al  $m^{-2}$ . This loading of alum was selected because it is within the range of those used in pilot tests and other eutrophic lakes (Rydin et al., 2000). During the course of the experiment, water samples (25 mL) were sampled every day in the overlying

water to measure the biogeochemical processes occurring in all sediment cores. This includes measurements of dissolved Al, Mn, Fe,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and total P concentrations before and after animal introduction. At the end of the 7-d incubation, the water layer was removed carefully and sediment was extruded with a piston and sectioned. The majority of the sediment was collected to measure Al, Mn, Fe, P, sulfur, water, and organic matter contents. Pore water was extracted from a subsample of the sediment by centrifugation and 0.45- $\mu\text{m}$  filtration of the supernatant for analysis of metals and nutrients.

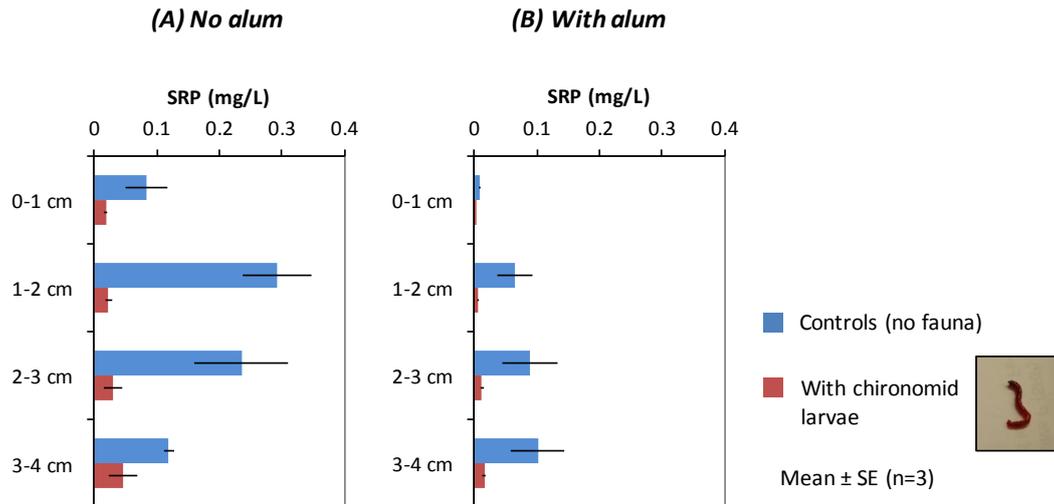
## 5.2. Principal Findings

In the non-alum amended cores, the SRP release from the sediment to the water column increased throughout the 1-week experiment (from day 0 to day 7, see Fig. 17A). The presence of chironomids in the non-alum amended cores induced higher release of SRP early in the test and then a lower release of SRP on days 4 and 7 in comparison to the control cores (no fauna). Such a result can be explained by the bioturbation activities (i.e., burrow building in the sediment) of chironomids in the sediment inducing a stimulation of the nutrient release from the sediment to the water column at the beginning of the experiment. The chironomids also ventilate their burrows to bring  $\text{O}_2$  and nutrients in depth (Van de Bund et al., 1994), which could have induced the increase of  $\text{O}_2$  concentrations deeper in the sediment and then decreased the release of SRP occurring in the anaerobic layers of the sediment. The addition of alum resulted in a total disappearance of SRP in the surface water of the control cores (Fig. 17B). The presence of chironomids in the alum-amended cores appeared to cause a small release of SRP later in the experiment, suggesting a potential reduction of alum effectiveness in the presence of bioturbating fauna. Our findings are in accordance with Andersen and colleagues (2006), who showed that after the addition of  $\text{AlCl}_3$  (adjusted to pH 7.5 with 2 M NaOH) to sediment cores, *Chironomus plumosus* larvae created burrows through the Al layer, which caused a significantly increased efflux of P from the Al treated sediment, due to limited contact of P with Al.

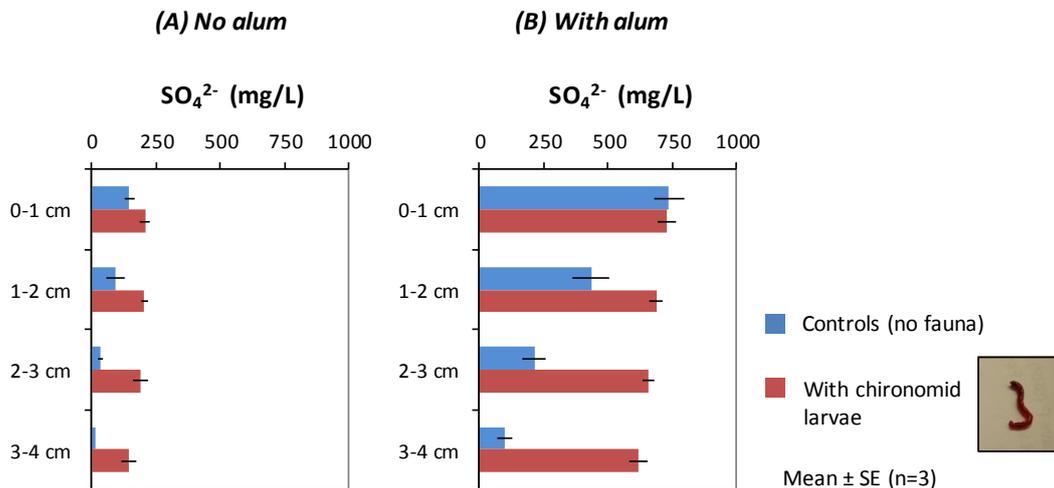


**Fig. 17.** Concentrations of soluble reactive phosphorus (SRP) in the surface water of the control cores (no fauna) and cores with the presence of chironomid larvae (A) without addition of alum and (B) with addition of alum (mean  $\pm$  1 SE,  $n=3$ ).

The concentrations of SRP in the pore water were significantly reduced with the addition of alum in the controls cores (Fig. 18). The presence of chironomid also significantly reduced the SRP concentrations in the pore water in comparison with controls with and without the addition of alum in the experimental cores (Fig. 18). Such results suggest that the ventilation activities of chironomid larvae may have increased the oxygen penetration in the sediment and then reduced the anaerobic release of SRP in the anaerobic sediment layers.



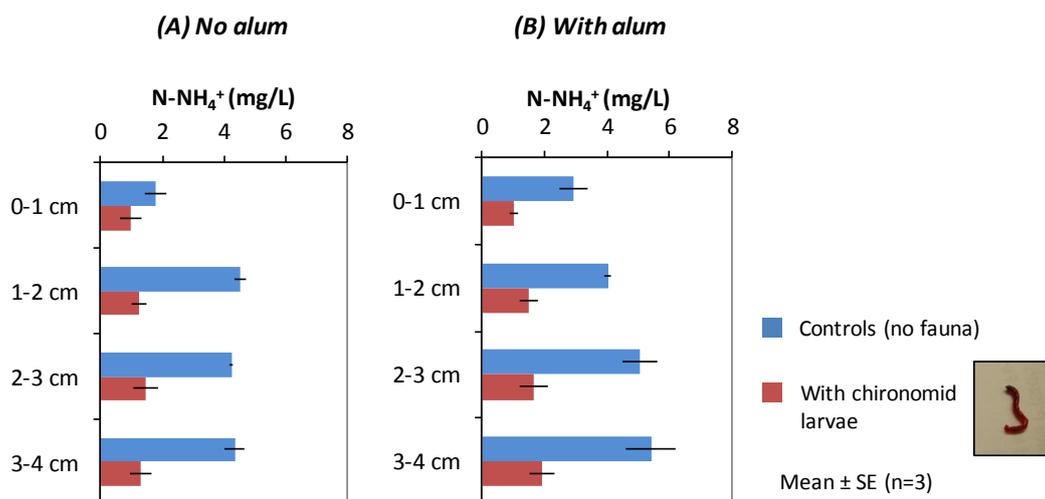
**Fig. 18.** Concentrations of soluble reactive phosphorus (SRP) in the pore water of the control cores (no fauna) and cores with the presence of chironomid larvae (A) without addition of alum and (B) with addition of alum (mean  $\pm$  1 SE,  $n=3$ ).



**Fig. 19.** Concentrations of sulfate ( $\text{SO}_4^{2-}$ ) in the surface water of the control cores (no fauna) and cores with chironomid larvae without addition of alum (A) and with addition of alum (B) (mean  $\pm$  1 SE,  $n=3$ ).

The addition of alum greatly increased the concentrations of  $\text{SO}_4^{2-}$  in pore water (i.e.,  $150 \pm 21$  vs.  $740 \pm 57$  mg/L  $\text{SO}_4^{2-}$  at 0–1 cm depth in the controls without and with addition of alum, respectively, Fig. 19). The concentrations of  $\text{SO}_4^{2-}$  also decreased with depth in both non-fauna treatments (with and without alum). The results of our mesocosm experiment support our second hypothesis that alum additions would increase sulfate levels in GLSM, which in turn would likely enhanced microbial sulfate reduction rates and generation of sulfide.

The presence of chironomid limited the anaerobic microbial transformation of  $\text{SO}_4^{2-}$  into toxic  $\text{S}^{2-}$  at depth with and without alum addition. Such result did not support our third hypothesis that alum additions would decrease invertebrate bioturbation in the sediment, and as a consequence, affect nutrient and metal cycling of GLSM. In contrast, the alum addition did not affect chironomid mortality in the sediment (data not shown) and the effect of chironomid bioturbation probably reduced the potential toxicity of increased sulfate concentrations in the alum-treated sediment.



**Fig. 20.** Ammonium ( $\text{NH}_4^+$ ) concentrations in the pore water of the control cores (no fauna) and cores with the presence of chironomid larvae (A) without addition of alum and (B) with addition of alum (mean  $\pm$  1 SE,  $n=3$ ).

As expected, the addition of alum did not affect the  $\text{NH}_4^+$  concentrations in the pore water of the control and chironomid cores (Fig. 20). The presence of chironomid greatly decreased the release of  $\text{NH}_4^+$  in the sediment, probably due to the increase of  $\text{O}_2$  penetration deeper in the sediment in comparison with the controls cores. Our results are in accordance with previous studies showing that chironomid bioturbation can stimulate aerobic microbial community through their bioturbation activities such as tube building and irrigation (Svensson and Leonardson, 1996; Svensson, 1997; Hansen et al., 1998).

## 6. SIGNIFICANCE OF THE PROJECT

Because P is often a limiting nutrient in freshwater ecosystems, loadings of P typically increase primary productivity and can lead to eutrophication and water quality degradation. GLSM is a typical example of a recreational lake that has been impacted for years by agriculture (cropland) and livestock operations in its watershed. This has resulted in high P loadings to the lake and subsequent blooms of toxic blue green algae. However, and unfortunately, there is paucity of information on the impacts of P loadings on temporal evolution of GLSM geochemistry and ecology. A recent paper has been published about the impact of agricultural activities on water quality of GLSM and streams in its watershed (Hoorman et al., 2008). This study found that the high P loadings to the lake are a major factor controlling algal blooms and water quality degradation (Hoorman et al., 2008). No data have been published on sediment geochemistry, metal concentrations, benthic communities, or even a simple mass balance for P in GLSM. The results of our study will enhance our knowledge and understanding of the ecological consequences of alum additions in GLSM and, in general, eutrophic freshwater ecosystems. Our findings will provide additional guidance and information to the lake resource managers, consultants and government agencies already working on the environmental issues at GLSM. This research also will provide a framework for other investigations and assessments of Ohio's GLSM restoration and watershed management.

## 7. PUBLICATIONS AND PRESENTATIONS

### 7.1. Manuscripts in preparation

Nogaro G., Burgin A.J., Schoepfer V., Konkler M., Bowman K., Hammerschmidt C.R. Alum treatment affects metal and biogeochemical cycling in hypereutrophic lake ecosystem. In preparation for *Journal of Environmental Quality*

Nogaro G., Burgin A.J., Taylor A., Konkler M., Schoepfer V., Hammerschmidt C.R. Can alum prevent harmful algal blooms and restore water quality in Grand Lake St. Mary's, Ohio? In preparation for *Journal of Environmental Quality*

Nogaro G., Burgin A.J., Taylor A., Marsh D., Lam K., Hammerschmidt C.R. Interactions between alum addition and invertebrate bioturbation on nutrient and metal releases in eutrophic lake sediments. In preparation for *Freshwater Biology*.

Taylor, A., Hammerschmidt, C.R., Burgin, A.J., Nogaro, G. Mass balance for phosphorous in eutrophic Grand Lake St. Mary's, Ohio. In preparation for *Water Research*.

### 7.2. Oral presentations in conferences and seminars

**Taylor A.**, Nogaro G., Burgin, A.J., Hammerschmidt C.R. (2012) Phosphorus budget and benthic flux in eutrophic Grand Lake Saint Mary's, Ohio. Geological Society of America North-Central Section, 46th Annual Meeting, April 23–24 2012, Dayton OH

**Nogaro G.**, Burgin A. J., Hammerschmidt C.R. (2012) Influence of alum addition on metal and nutrient cycling in Grand Lake Saint Mary's, Ohio. Environmental Science Graduate Program's spring seminar series, Ohio State University, April 6 2012, Columbus OH

**Nogaro G.**, Hammerschmidt C.R. Burgin A. J. (2011) Alum influence on metal and nutrient cycling and benthic communities in a shallow eutrophic lake. Annis water Resources Institute seminar series, Grand Valley State University, July 22 2011, Muskegon MI

**Nogaro G.**, Hammerschmidt C.R. Burgin A. J. (2011) Influence of alum addition on metal and nutrient cycling in Grand Lake Saint Mary's, Ohio. North American Benthological Society (NABS) meeting, May 22-26 2011, Providence RI

## 8. STUDENT SUPPORT

This project provided funding and research opportunities for one undergraduate student (Miss Deepthi Nalluri, biology major) and two graduate students (Ms. Astrea Taylor and Valerie Schoepfer, M.S. Earth & Environmental Sciences) at WSU. These students participated in the field (water and sediment sampling) and laboratory experiments, which afforded them new opportunities for research and professional development. We expect that participation in this collaborative research effort will result in a cohort of broadly-trained, integrative scientists with expertise in geochemistry, microbiology, and ecology.

## 9. NOTABLE AWARDS AND ACHIEVEMENTS

A Phosphorus Budget for Grand Lake Saint Mary's, Ohio (\$9,948) Funded **by the Wright State University Research Council**. C. R. Hammerschmidt (lead), A. J. Burgin, G. Nogaro.

Phosphorus budget and benthic flux in eutrophic Grand Lake Saint Mary's, Ohio (\$750) Funded **by Graduate Student Association, Wright State University**. A. Taylor.

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