

# 2011 annual report

U.S. GEOLOGICAL  
SURVEY

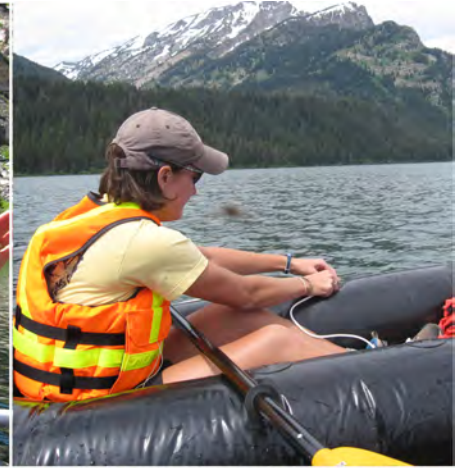
NPS AIR RESOURCES  
DIVISION

INSTAAR, UNIVERSITY  
OF COLORADO

UNIVERSITY OF  
ALBERTA

GRAND TETON  
NATIONAL PARK

RM-CESU



## Atmospheric deposition of inorganic nitrogen in Grand Teton NP: **determining biological effects on algal communities in alpine lakes**

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## Highlights

The year 2011 was an intensive period of a second year fieldwork, sample processing, data analysis and manuscript preparation. Megan Otu, postdoctoral fellow, completed tasks directed towards the study objectives using the facilities at INSTAAR, University of Colorado. Fieldwork in 2011 in GRTE included successfully obtaining additional sediment cores from two lakes (Phelps and Bradley) and retrieving sediment traps from Whitebark Moraine Pond. The sediments from seven lakes (Delta, Surprise, Amphitheater, Ramshead, Holly, Whitebark Moraine, and Grizzly) cored during the 2010 field season were processed by Otu. She analyzed data from the first set of prepared a manuscript for publication. Our preliminary results include that all sediment stratigraphies from the GRTE lakes exhibit a pattern of declining  $\delta^{15}\text{N}$  and C:N ratio that suggest a regional change in nitrogen inputs during the past 150 years. The increase in nitrogen relative to carbon deposition concurrent with an average isotopic shift of 2.2 ‰ suggests both an increase in N supply relative to C fixation rates and a shifting source of N to the system. The  $\delta^{15}\text{N}$  and C:N trends were nearly static before 1880, as the atmospheric deposition of DIN was limited to the pre-industrial N cycle and  $\text{CO}_2$  concentrations were relatively unimpacted by human disturbances.

### Outline

- A) 2011 Project Activities
- B) Preliminary Results
  - a. Lake Nutrient Status
  - b. Paleolimnology
  - c. Diatom Species Composition and Abundance
  - d. Sediment Geochemistry and Stable Isotopes
  - e. Discussion
- C) Deliverables in Progress and Completed
- D) Synergistic Activities
- E) Remaining Tasks and Challenges

## A) 2011 Project Activities

The second year of the project continued with an intensive schedule of laboratory processing, data analysis, scientific presentations and preparation of manuscripts. Megan Otu led the efforts, until her one year position was completed in July 2011. Field and lab activities included a number of participants:

Megan Otu	- Postdoctoral Fellow, University of Colorado
Sarah Spaulding	- co-PI, US Geological Survey
Alexander Wolfe	- co-PI, University of Alberta
Jill Baron	- co-PI, US Geological Survey
Emma Jones	- MS student, University of Alberta
Brooke Osbourne	- PhD student, Colorado State University
Chad Whaley	- Park Technician, Grand Teton National Park
Marina Potapova	- Curator, Academy of Natural Sciences of Philadelphia
Sue O'Ney	- Park Biologist, Grand Teton National Park
Jeff Otu	- Volunteer, University of Colorado
Tamara Blett	- National Park Service, Air Resources Division
John Vimont	- National Park Service, Air Resources Division
Bret S.	- National Park Service, Air Resources Division

## B) Preliminary Results

### a. Lake Nutrient Status

Lake water was circumneutral and oligotrophic with low conductivity, ion and nutrient concentrations (Table 1). Transparency in most lakes was very high, except for Delta Lake, which was turbid from suspended glacial flour. Both Grizzly and Holly lakes support fish and are known to have been stocked with Yellowstone cutthroat trout, *Oncorhynchus clarkia bovieri*, in the early 20<sup>th</sup> century (Hazzard 1931). The other lakes are considered to lack fish, although three brook trout, *Salvelinus fontinalis*, were captured during a gill net survey of Ramshead Lake in 1994. Since that time, however, fish have not been reported.

Parameter	Grizzly	Holly	Whitebark Moraine	Ramshead	Lake of the Craggs	Delta	Amphitheather	Surprise
Latitude (°N)	43.8030	43.7927	43.7884	43.7767	43.7753	43.7325	43.7297	43.7285
Longitude (°W)	-110.810	-110.7980	-110.7943	-110.7641	-110.7707	-110.7729	-110.7813	-110.7772
Elevation (m)	2810	2870	2801	2895	2917	2748	2957	2915
Surface Area (ha)	4.9	3.1	1.1	1.1	4.5	2.8	1.9	0.9
Catchment Area (ha)	12018	34628	7122	4791	17094	18415	7200	997
CA:SA	2453	11170	6475	4563	3824	6648	3850	1061
Fish Status	yes	yes	no	maybe	no	no	no	no
Water Depth (m)	7.6	8.5	3.7	6.6	19.1	9.4	8.5	7.0
Secchi Disk (m)	5.5	5.7	3.7	4.8	NA	0.8	7.6	7.0
pH	6.8	6.8	6.7	6.6	6.6	6.5	6.5	6.4
Conductivity (uS/cm)	15.6	13.3	11.2	9.9	9.9	9.5	6.7	6.4
ANC (ueq/L)	119	99	87	77	76	60	50	50
DOC (mg/L)	0.51	0.59	1.78	0.51	0.49	0.34	0.57	0.79
NH4+ (umol/L)	0.063	0.610	0.063	0.952	0.529	0.063	0.063	0.292
Ca++ (umol/L)	48.4	36.3	30.6	27.8	29.1	23.8	16.0	15.2
Cl- (umol/L)	2.2	2.7	2.4	2.5	3.4	3.3	2.3	3.0
NO3- (umol/L)	1.77	0.01	0.01	3.21	5.14	12.43	1.68	0.01
SO4= (umol/L)	10.6	10.6	7.4	4.4	4.7	5.4	3.1	3.3
PO4-(umol/L)	0.022	0.022	0.027	0.028	0.018	0.042	0.030	0.017
Si (umol/L)	27.9	43.1	16.6	19.3	24.3	15.8	14.6	13.9
TN (umol/L)	5.7	3.8	7.7	9.5	10.6	13.1	5.2	5.2
TP (umol/L)	0.079	0.113	0.155	0.128	0.118	0.114	0.078	0.097
TN:TP (molar)	72	33	50	74	90	115	67	54
DIN:TP (mass)	45.4	3.3	0.4	54.6	89.9	219.2	43.6	2.0

Table 1. Lake physical and chemical characteristics July to August 2010, Grand Teton National Park, WY. Water chemistry presented is the mean of three water column samples from surface (0.3 m), mid (2-3 m) and bottom (0.5 m above maximum depth). Fish status based on Stephens (2007) where Yellowstone cutthroat trout found in Grizzly and Holly Lake and three brook trout were found in 1994 survey (anecdotal). Whitebark Moraine Pond was not included in the fish survey.

A latitudinal gradient in conductivity (linear regression  $r^2=0.79$ ) and ANC ( $r^2=0.89$ ) is present from Grizzly Lake to the north to Surprise Lake to the south (15.6 - 6.4  $\mu\text{S cm}^{-1}$  and 119 - 50  $\mu\text{eq L}^{-1}$ , respectively). The same N-S gradient exists in calcium ( $r^2=0.81$ ) and sulphate ( $r^2=0.64$ ) concentrations from Grizzly to Surprise Lake (48.4 - 15.2  $\mu\text{mol L}^{-1}$  and 10.6 - 3.3  $\mu\text{mol L}^{-1}$ , respectively). Silica concentrations have a weaker N-S trend ( $r^2=0.46$ ), with concentrations measuring 13.9 - 43  $\mu\text{mol L}^{-1}$ .

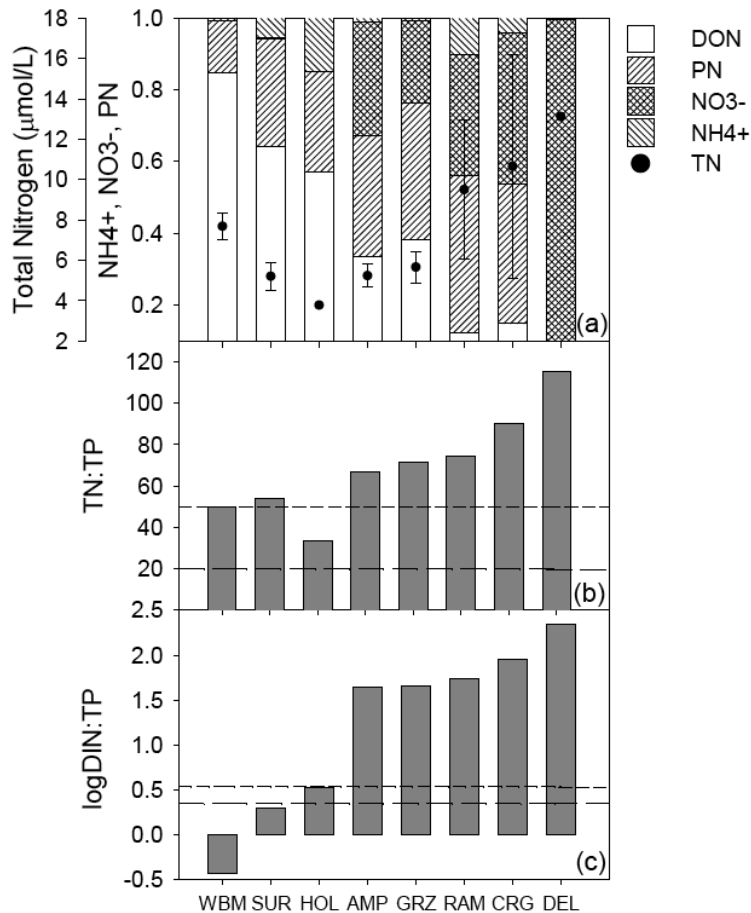


Figure 1. Total nitrogen speciation for each of the eight sampling sites in the Grand Teton National Park, WY. (a) Total nitrogen on the outside left vertical axis is represented as a proportion of the N species (from the top down) ammonia ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), particulate N (PN) and dissolved organic N (DON). (b) Total nitrogen (TN) to total phosphorus (TP) molar ratios for each of the GRTE lakes, the long dashed line at 20 denotes the threshold below which phytoplankton were not found to be P deficient and the short dashed line at 50 denotes phytoplankton above which P deficiency was found in freshwater lakes (Guildford and Hecky 2000). (c) Dissolved inorganic nitrogen (DIN) to TP mass ratios are presented on a log scale with  $\log 2.2$  denoting 50% probability of P limitation and  $\log 3.4$  denoting 75% probability of P limitation (Bergström 2010).

Essential growth nutrients, N and P lacked a latitudinal trend, but showed other patterns. The total N concentrations (mean  $7.6 \pm 3.2 \mu\text{mol L}^{-1}$ ) amongst lakes varied more than the total P concentrations ( $0.11 \pm 0.025 \mu\text{mol L}^{-1}$ ). The relative proportion of N constituents ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , particulate N and dissolved organic nitrogen DON) showed a range of speciation (Figure 1a). The highest TN values were in glacial-fed Delta Lake, with over 95% in the form of  $\text{NO}_3^-$ . In contrast, 85% of the TN in Whitebark Moraine Pond was in the form of DON. There is a trend with DOC and TP showing a positive linear relationship with the catchment area to surface area ratio at  $r^2=0.76$  and  $0.63$  respectively. The highest TP concentrations were in Whitebark Moraine Pond, largely composed of DOP. The

lowest TP concentrations were in Amphitheater Lake, composed predominantly of particulate, bound P.

TN:TP (molar) ratios can be used to characterize the relative availability of N to P in the basin (Figure 1b). When N availability is high, phytoplankton productivity in freshwater bodies can become P limited. In North America, TN:TP values above 50 (molar) were found to be P limited systems. Based on those findings, nearly all lakes in GRTE are P-limited, except Holly Lake. Bergstrom (2010) found that DIN:TP (mass) ratios had better predictability than TN:TP ratios with values above 3.4 having a 75% probability of predicting P limitation during fertilization experiments. Since DON is the dominant species of N in White Bark Moraine Pond and Surprise Lake, the DIN:TP values are low ( $\leq 3.4$ , Figure 1c) and potentially N-limited during the post-snowmelt season in July and August.

#### b. Paleolimnology

During the 2011 field season, we observed that surface waters from the mid-elevation lakes, Phelps and Bradley, contained the species *Asterionella formosa*. This species of diatom is considered a marker of mesotrophic nutrient conditions. This observation was a bit of a surprise, as we expected that high elevation lakes would be the most vulnerable to deposition of atmospheric nitrogen. We obtained cores of sediments from Phelps and Bradley lakes to include paleolimnological reconstruction of diatoms and nutrient status in these lakes. Samples from the cores are currently being processed for age chronology, sediment chemistry and diatom species composition. This work will continue in coming months.

Results from the 2010 field season are summarized here. Sediment records could not be recovered from Lake of the Crags, and thus paleolimnological reconstructions were carried out on the seven remaining lakes. Sediment chronology was based on the CRS model applied to the  $^{210}\text{Pb}$  activity profiles (Figure 2). Overall, the background  $^{210}\text{Pb}$  activities from the GRTE lakes were considerably high (mean  $0.18 \text{ Bq g}^{-1}$ ), ten times what may be expected of an oligotrophic lake (Larder per. com.). Grizzly Lake had the highest  $^{210}\text{Pb}$  activity at  $0.57 \text{ Bq g}^{-1}$ . High background levels were likely the result of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  in the rock and soils within the catchment or from high  $^{222}\text{Rn}$  in groundwater. The background measures were also more variable between sites, but this is to be expected if the radium is very high. In Holly Lake, sediment  $^{210}\text{Pb}$  did not measure background levels, so background values from Whitebark Moraine Pond were used as both lakes share similar levels of  $^{210}\text{Pb}$  activity.

Sedimentation rates (Figure 2) were all very low and consistent with similar studies of high alpine lakes. Sedimentation rates in Whitebark Moraine Pond and Surprise Lakes remained relatively unchanged as compared to the large sedimentation events that occurred in Ramshead and Holly lakes or the trend in rising sedimentation rates in Grizzly (since ~1994) and Delta (~1993) lakes.

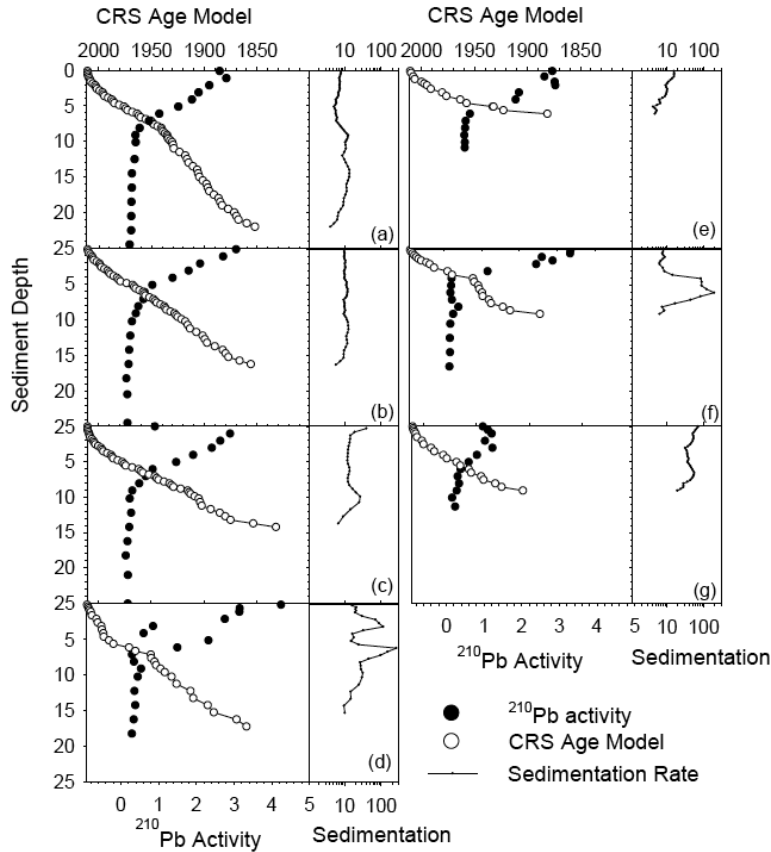


Figure 2.  $^{210}\text{Pb}$  activity decay profiles ( $\bullet$ ,  $\text{Bq g}^{-1}$ ), constant rate of supply CRS age model ( $\circ$ , date) and sedimentation rate (line plot,  $\text{g m}^{-2} \text{yr}^{-1}$ ) for sediment cores recovered from (a) Whitebark Moraine Pond, (b) Surprise, (c) Amphitheater, (d) Holly, (e) Grizzly, (f) Ramshead, and (g) Delta Lakes during July and August 2010 from Grand Teton National Park, WY. Note the sedimentation rates are shown in log scale plot.

### c. Diatom species composition and abundance

All diatom assemblages from lakes cored in 2010 were dominated by benthic taxa with relative abundances sorted by N:P values from lake water chemistry (Figures 3 and 4). Delta Lake did not have an enumerable preserved diatom fossil record. Whitebark Moraine Pond contained a high abundance of *Staurosirella pinnata* (Ehrenberg) Williams et Round, *Staurosira construens* var. *venter* (Ehrenberg) Hamilton and to a lesser extent *Pseudostaurosira brevistriata*

(Grunow in Van Heurck) Williams et Round.

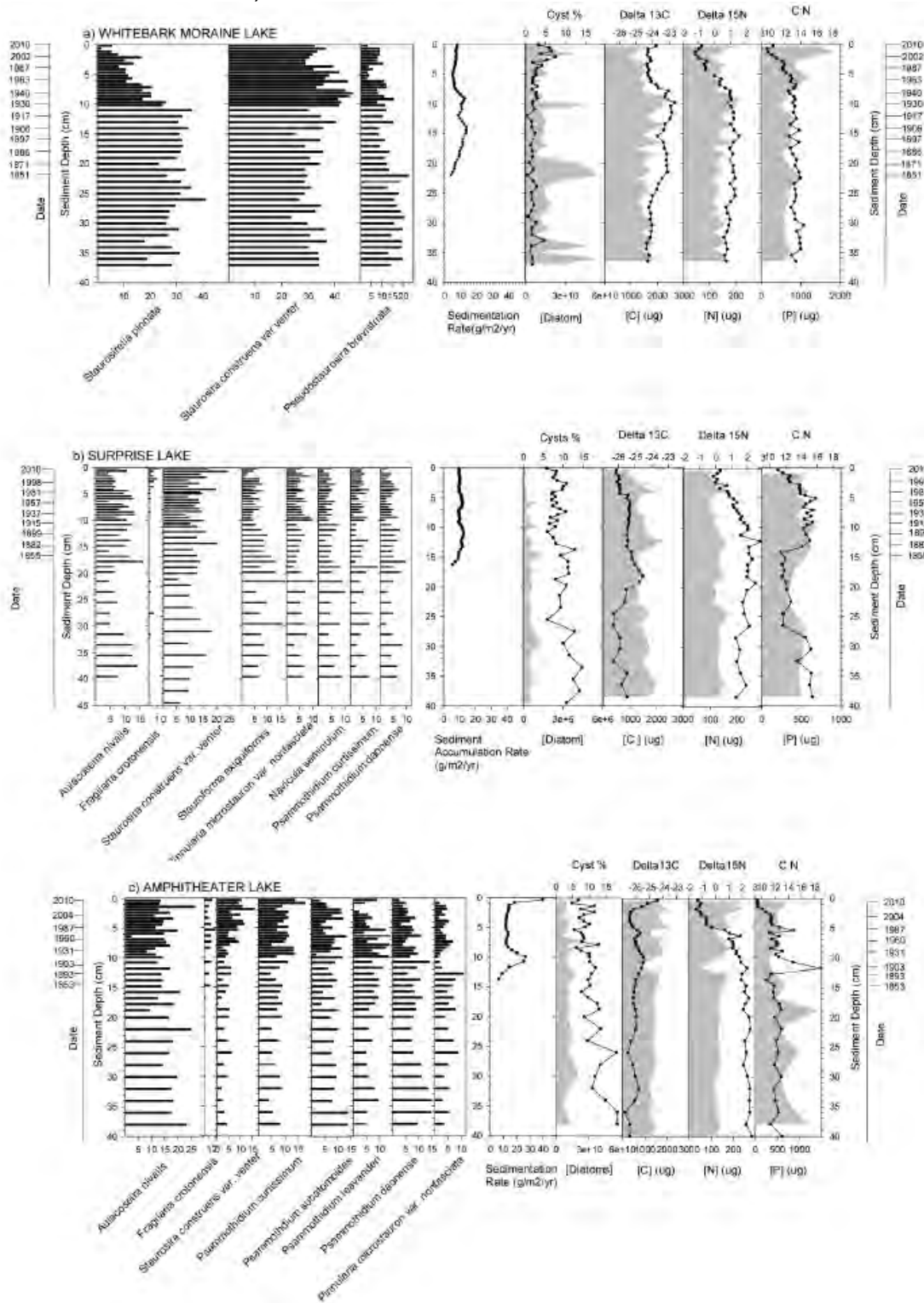


Figure 3. Plots of a) Whitebark Moraine Pond, b) Surprise Lake and c) Amphitheater Lake showing sediment age chronology, dominant diatom species, sedimentation rate, percent chrysophyte cysts, total diatom abundance,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  stable isotopic composition, total carbon, total nitrogen, C:N ratios and total phosphorus.



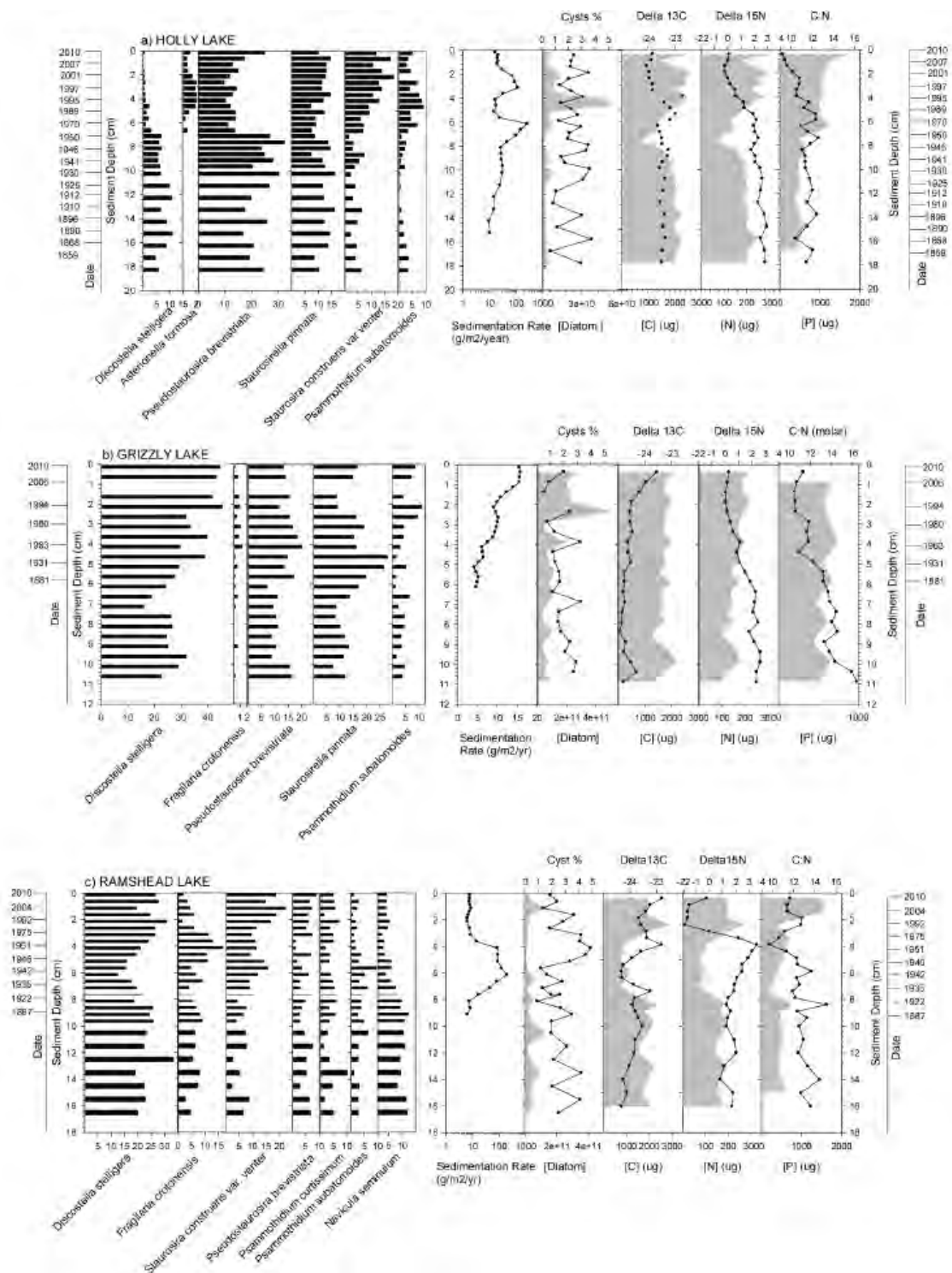


Figure 4. Plots of a) Holly Lake, b) Grizzly Lake and c) Ramshead Lake showing sediment age chronology, dominant diatom species, sedimentation rate, percent chrysophyte cysts, total diatom abundance,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  stable isotopic composition, total carbon, total nitrogen, C:N ratios and total phosphorus.



Amphitheatre and Surprise Lakes share a similar diatom assemblage likely because of the hydrological connection from the outlet at Amphitheater Lake, which feeds into Surprise Lake downstream. Both lakes have a high number of diatom taxa represented because percent abundances are < 10% that include *Stauroforma exiguiformis* (Lange-Bertalot) Flower et al., *Aulacoseira nivalis* (W. Smith) English et Potapova and a diversity of monoraphid *Psammothidium* species.

*Aulacoseira nivalis* (W. Smith) English et Potapova and *Discostella stelligera* (Cleve et Grunow) Houk et Klee were one a few planktonic taxa that were present in greater relative abundances. *Aulacoseira nivalis* was only present in Amphitheatre and Surprise Lakes at 6.8 to 8.7 % abundance and < 1% at all other sites. *Discostella stelligera* (Cleve et Grunow) Houk et Klee, was represented at 15 to 40 % relative abundance in Holly, Grizzly, and Ramshead lakes.

*Fragilaria crotonensis* and *Asterionella formosa* are mesotrophic planktonic diatoms found in many anthropogenically eutrophied lakes. *Fragilaria crotonensis* was present in Surprise, Amphitheater and Grizzly Lakes at < 1% and in Ramshead Lake at 6.8 % total core abundance. *Fragilaria crotonensis* was found in sediments dating before 1850 with no discernable population trend. *Asterionella formosa* was present only in sediment samples from Holly Lake during ~1985 to 2010, however relative abundance does not exceed 3%. Overall, diatom community composition does not indicate a shift towards planktonic mesotrophic taxa, but rather a relatively unaltered benthic diatom community composition during the past 150 years and earlier.

#### d. Sediment geochemistry and stable isotopes

Comparison amongst the concentrations of phosphorus, nitrogen and carbon and the C:N (molar),  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  stable isotopic composition of each sediment core (Figs 3 and 4) showed that in all sediment cores C:N (except Delta Lake) and  $\delta^{15}\text{N}$  decline.  $\delta^{15}\text{N}$  plots followed a trend in depletion in all lakes, from pre-industrial values of up 2.7 ‰ to surface sediments of -2.2 ‰, an average  $\delta^{15}\text{N}$  depletion 2.2 ‰ during the past 150 years. At the same time, there was also a coincident decline in C:N ratios from an average of 13.0 to 10.5 starting around ~1960 until present. C:N ratios in Delta lake were not discernable. The large fluctuations in inorganic deposition in Ramshead Lake that increased sedimentation rates during ~1942-1951 appear to have impacted the biogeochemical trends.

Sedimentary concentrations of P, C and N varied considerably amongst lakes, whereas nutrient stoichiometry was consistent. Concentrations of P increased in

most lakes but Amphitheater and Grizzly Lakes, while concentrations of C and N have gradually increased in Holly, Amphitheater, Grizzly, Ramshead and Delta Lakes over time. Sedimentary molar ratios of C:P and N:P were on average  $7.3 \pm 1.0$  and  $0.58 \pm 0.09$  respectively for all GRTE lake sediments except Delta Lake ( $1.6 \pm 0.5$  and  $0.18 \pm 0.05$ ). Sedimentary ratios were an order of magnitude lower than water column measures and do not suggest P limitation.

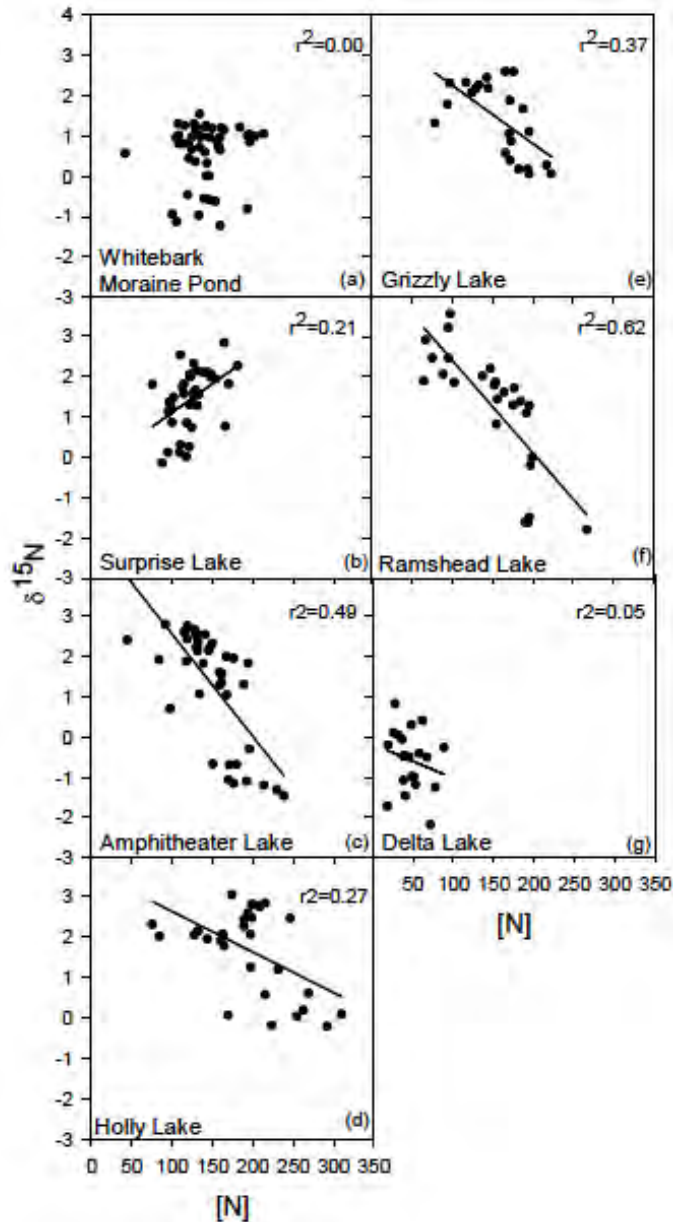


Figure 5. Trends in the concentration of nitrogen ( $\mu\text{g g}^{-1}$ ) relative to  $\delta^{15}\text{N}$  (per mil) isotopic signature of bulk matter in sediment cores from (a) Whitebark Moraine Pond, (b) Surprise, (c) Amphitheater, (d) Holly, (e) Grizzly, (f) Ramshead and (g) Delta Lakes from GRTE, WY. Linear regressions and  $r^2$  values presented on each plot.

## e. Discussion

All sediment stratigraphies from the GRTE lakes exhibit a pattern of declining  $\delta^{15}\text{N}$  and C:N ratio that suggest a regional change in nitrogen inputs during the past 150 years. The increase in nitrogen relative to carbon deposition concurrent with an average isotopic shift of 2.2 ‰ suggests both an increase in N supply relative to C fixation rates and a shifting source of N to the system. The  $\delta^{15}\text{N}$  and C:N trends were nearly static before 1880, as the atmospheric deposition of DIN was limited to the pre-industrial N cycle and  $\text{CO}_2$  concentrations were relatively unimpacted by human disturbances. As settlement in the United States increased along with industry and agriculture after 1880, an additional supply of DIN with a depleted  $\delta^{15}\text{N}$  signature was supplied. However, the increased availability of N (of the same or lighter isotopic signature) would also favour greater kinetic isotopic fractionation, as autochthonous primary producers will preferentially uptake the lighter  $\delta^{14}\text{N}$  isotope when N limitation is diminished. An increased  $\text{N}_2$  fixation that could be contributing to the  $\delta^{15}\text{N}$  decline, however the values would approach 0 ‰ air, and not fall below 0 ‰, as in these GRTE sedimentary records. Phytoplankton tows from each GRTE sampling sites had an absence of heterocystous,  $\text{N}_2$  fixing algal taxa that could be contributing substantially to the N budget and  $\delta^{15}\text{N}$  signature. Thus, sedimentary trends in declining  $\delta^{15}\text{N}$  and C:N are likely reflective of changing N<sub>r</sub> deposition trends, irrespective of diagenesis or  $\text{N}_2$  fixation.

The effects of sediment diagenesis were not believed to be impacting these stratigraphic trends, as deeper sediments are often exposed to greater preferential release of N impacting C:N ratios, particularly with the release of the heavier  $\delta^{15}\text{N}$  isotope. Organic matter diagenesis in surface sediments generally proceeds under anoxic conditions where easily degradable proteins and carbohydrates that are  $\delta^{15}\text{N}$  enriched would be released first, leaving less reactive humic substances and lipids that are  $\delta^{15}\text{N}$  depleted to remain. Wolfe et al. (2002) examined the fidelity of C:N in sediment traps and sediment records from Sky Pond and Lake Louise, Rocky Mountain National Park using organic matter fluorescence and found that rapid alteration of the C:N ratio occurred within the water column and that C:N was a robust proxy of organic matter in sediment records, where burial can stabilize ratios. Wolfe et al (2002) concluded C:N is a faithful tracer of increased autochthonous organic matter deposition during elevated aquatic productivity from increased N<sub>r</sub> atmospheric deposition (Wolfe 2002 and Kanassanen et Jaakola 1985).

Sediment diagenesis, however, may need further investigation. Work in late 2011 will be directed at resolving the relationship between  $\delta^{15}\text{N}$ , N, and diatom community change in the sediment record. The effects of diagenesis on GRTE sediments may be characterized by comparing the trend in  $\delta^{15}\text{N}$  relative to N concentrations (Figure 5). Whitebark Moraine Pond and Surprise Lakes have the lowest N:P ratios and show no trend between N concentrations and  $\delta^{15}\text{N}$ . Diagenesis is believed to impact the pattern of C:N and  $\delta^{15}\text{N}$  signature of

sediments and anoxic diagenesis generally proceeds with the preferential loss of  $\delta^{15}\text{N}$  rich organic matter. There was a strong negative trend in the snow fed lakes with moderate to high N:P ratios, with more recent sediments characterized by lower  $\delta^{15}\text{N}$  values and higher N concentrations in Holly ( $r^2=0.27$ ), Amphitheater ( $r^2=0.49$ ), Grizzly ( $r^2=0.37$ ) and Ramshead Lakes ( $r^2=0.62$ ). This trend is contrary to what might be expected during diagenesis of anoxic sediments. The recent increased N concentrations also attests to the increased N availability in these basins, which are largely dependent on wet and dry atmospheric DIN deposition for N inputs, having poorly developed soils and restricted catchment sizes.

The poor fit between  $\delta^{15}\text{N}$  and N concentrations of Delta Lake was expected, as N is delivered from both the Teton Glacier meltwater that delivers stored  $\text{NO}_3^-$ , and to a lesser extent from direct atmospheric  $\text{N}_r$  deposition. In general, N concentrations in the Delta Lake sediments have increased with depleted  $\delta^{15}\text{N}$  signatures, however over very low N concentration range (18-88  $\mu\text{g N g}^{-1}$ ).

The trend in depleted  $\delta^{15}\text{N}$  and C:N across GRTE lakes, of which all are dominated by snowpack melt hydrology, represent regional  $\text{N}_r$  deposition trends. The high amount of inorganic deposition in Ramshead Lake increased the lake specific variability and has been eliminated from the  $\delta^{15}\text{N}$  averaged trends for this reason. The average  $\delta^{15}\text{N}$  values from the five GRTE lakes present a trend comparable to the  $\delta^{15}\text{N}_{\text{NO}_3^-}$  Summit Greenland ice core record. There is a difference in the rate of change of the  $\delta^{15}\text{N}$  trends between the two records, with sediment records showing an increase during ~1975 to 2000 and  $\delta^{15}\text{N}_{\text{NO}_3^-}$  ice records during 1950-1980. Lake sediment  $\delta^{15}\text{N}$  declines from only 2.8 to -1.1 ‰ and the ice core  $\delta^{15}\text{N}_{\text{NO}_3^-}$  shifts from 14 to -2 ‰. The magnitude of the  $\delta^{15}\text{N}_{\text{NO}_3^-}$  is five times greater than  $\delta^{15}\text{N}$  in lake sediments, likely because of in-lake effects. Biotic N cycling within the water column utilizes the most bio-available N species and selectively fractionates  $\delta^{15}\text{N}$ . Yet, the overall lake sediment trends show a similar trend in  $\delta^{15}\text{N}$  depletion. Both records capture northern hemispheric  $\text{N}_r$  pollutants and track the rapid increase of fossil fuel emissions after 1970.

The source of alpine  $\text{N}_r$  deposition to the GRTE may have a more acute response to the effect of local agricultural emissions, which are known to have increased rapidly after 1974 (NADP) with increased meat and dairy production, crop burning and fertilization (Figure 7c). High ammonia emissions from the Snake River Valley, ID only 150 km from GRTE were measured from satellite imagery. Ammonia concentrations are steadily increasing during the past 20 years with agricultural release of  $\delta^{15}\text{N}$  depleted ammonia. The Snake River Plain is a region of high ammonia emissions due to agricultural expansion. Ammonia can be readily consumed by primary producers with minimal fractionation during cellular uptake, which likely contributes further to the trend in depleted  $\delta^{15}\text{N}$  sedimentary signatures.

In the GRTE sediment records, the presence of *F. crotonensis* and *A. formosa* does not appear to be linked with other  $\text{N}_r$  depositional trends, and could be

linked to species introductions during early exploration of these basins<sup>37</sup>. However, Saros and colleagues (2010) found the same trend in low relative abundances of *F. crotonensis* and *A. formosa* in Snyder and Old Man Lakes from Glacier National Park. Authors suspected that the high DIN:TP values (11.2 and 18.2 respectively) meant they were severely P limited and could not respond to excess N from Nr deposition. In GRTE, the P sediment record does not indicate that P is a limiting factor for primary production and requires alternative explanations. The same diatom trend occurred in the Uinta Mountains, Utah where copper mining activities after 1860 increased dust to the region and is suspected of providing an alternate source of nutrients. Large-scale mining practices in southeast Idaho rapidly expanded in 1900s and were associated with extensive waste dumps, ore stockpiles, tailings ponds, roads, railroads and expansion of facilities. Nutrient inputs from dust could support the presence of mesotrophic *F. crotonensis* and *A. formosa* in the sedimentary records, but further analyses of heavy metals associated with mining would better elucidate this relationship.

#### f. Preliminary Conclusions

The impact of this regional Nr deposition does not appear to affect each lake similarly, but sediment records follow a series of ecological impacts along a continuum of nutrient enrichment. This response continuum starts from a shift in the relative availability of growth limiting nutrients (N and P) to greater primary production, accelerated rates of primary production and increased sedimentation rates. In many other alpine lakes, benthic communities were replaced by planktonic mesotrophic taxa, such as *Asterionella formosa*, as nutrient enrichment can result in benthic habitat loss due to reduced light penetration and self-shading that shift the ecological functioning of an aquatic system.

Ratios of DIN:TP related best to Nr enrichment trends in GRTE lakes, as compared to the previous use of ANC to determine lake sensitivity to Nr loading. High nitrate concentrations drive the DIN:TP trend, which appears to better represent the nutrient enrichment continuum. High  $\text{NO}_3^-$  concentrations may not be due to  $\text{NO}_3^-$  deposition alone. Alpine sites exposed to an excess DIN deposition and acidification of soils led to leaching of nitrate into the aquatic ecosystem. In ultra-oligotrophic Lake Superior, an in depth assessment of the N budget found that the rising  $\text{NO}_3^-$  concentrations were not due solely to catchment inputs or direct DIN deposition inputs, but rather to reduced  $\text{N}_2$  loss from denitrification. As a result,  $\text{NO}_3^-$  concentrations accumulated and  $\text{NO}_3^-:\text{PO}_4^{3-}$  ratios climbed to 10,000. In some GRTE lakes,  $\text{NO}_3^-$  measures were below detection and limit the use of  $\text{NO}_3^-$  alone to establish an Nr gradient, but greater  $\text{NO}_3^-$  concentrations were reflective of greater Nr enrichment in sediment records. Continued monitoring of DIN:TP may help to assess changes in water quality from prolonged Nr deposition over time.

Both TN:TP and to a greater extent DIN:TP predict that P limitation would be controlling phytoplankton biomass in the GRTE lakes, but sedimentary records do not support a trend in P limitation. As a result, recent increased Nr atmospheric deposition has not shifted these oligotrophic systems from a pre-historic N limitation state to present day P limitation, rather N limitation likely still prevails in these aquatic ecosystems.

GRTE benthic diatom community composition is likely buffered from changing water chemistry because of the nutrient cycling that occurs at the substrate surfaces. Diatoms do not presently exhibit discernable changes due to nutrient inputs, but prolonged exposure to Nr deposition could trigger a critical load response with larger-scale shifts from benthic to planktonic taxa, which will have a much greater ecological impacts to the food web. Presently, the closest NADP site to GRTE (Gypsum Creek) measured  $3.51 \text{ kg TIN ha}^{-1} \text{ yr}^{-1}$ , which is a value well above the  $1.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$  established as the critical load in the Rocky Mountain National Park or  $1.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$  in the Sierra Nevada and Greater Yellowstone Ecosystem. These ecological changes have been seen previously in the Rocky Mountain National Park, the Sierra Nevada and Beartooth Mountain Ranges, and serve as a warning of what may be in the future should mitigation of DIN emissions fall off target.

#### **D) Deliverables in Progress and Completed**

Megan Otu presented preliminary results at the Society of Canadian Limnologists conference, January 2011, Toronto, Canada.

Megan Otu and Sarah Spaulding completed ten taxon pages of species from GRTE lakes for the Diatoms of the United States, a national online flora. See: [http://westerndiatoms.colorado.edu/about/project/1501/atmospheric\\_deposition\\_of\\_nitrogen\\_and\\_its\\_effects\\_on\\_diatoms](http://westerndiatoms.colorado.edu/about/project/1501/atmospheric_deposition_of_nitrogen_and_its_effects_on_diatoms)

Megan Otu presented preliminary results at the Greater Yellowstone Area Critical Loads Workshop, April 5-6, 2001, Jackson, Wyoming.

Sarah Spaulding was an invited speaker for a special session on nitrogen biogeochemistry, American Chemical Society, August 2011, Denver CO. Spaulding, S.A., Otu, M., Baron, J. and Wolfe, A.P. Response of sensitive freshwater ecosystems to reactive nitrogen deposition in western North America.

Otu, M., Spaulding, S.A., Wolfe, A.P. and Baron, J. Deposition of atmospheric reactive nitrogen on high elevation western lakes and the response of diatoms. (in preparation for Ecological Applications).

Otu, M., Spaulding, S.A. and Potapova, M. Diatom flora of Grand Teton National Park (in preparation for Iconographia Diatomologica).

## **E) Synergistic Activities**

Sarah Spaulding and Janice Brahney, Ph.D. candidate at University of Colorado, are collaborating on the sediment and diatom records of GRTE and the Wind River Range of Wyoming. The two regions present an opportunity to examine the depositional signals and response across a broader region. A joint manuscript is planned as a result of the collaboration.

Jill Baron and students are working on chemical and microbial analyses of the soils/protosoils from Teton watersheds. The group plans to examine NO<sub>3</sub>, NH<sub>4</sub>, DOC, TON in leachate, %C, %N, microbial biomass, qPCR for nitrifiers, and net and gross N mineralization rates.

Heather Mosher, M.S. student at University of Alberta, is analyzing organic compounds from tree cores from trees surrounding the study lakes. She is working with Alex Wolfe to develop methods to quantify the  $\delta^{15}\text{N}$  fractionation in wood, across species, and determine if the record is correlated to changes recorded in lake sediments.

Emma Jones, M.S. student at University of Alberta, is evaluating the Whitebark Moraine Pond sediments for charcoal, and therefore, fire history, by VIS-NIR spectroscopy. The work will develop a calibration of the quantitative abundance of charcoal in lake sediments and evaluate this approach in comparison to traditional approaches. The results will address the relationship between fire, DOC and algal impacts.

Mabruka Abubeira, Ph.D. student at Colorado State University, is working with Jill Baron. Mabruka is considering reconstruction of the chironomid (midge larvae) paleolimnological record in Whitebark Moraine Pond to as a proxy for regional temperature change in GRTE. She may also measure uv-absorbance from Cladoceran fossil exuviae extracted from sediments, using laser-scanning confocal microscopy. This will inform on changes in ultraviolet radiation on the lakes over time.

## **F) Remaining Tasks and Challenges**

Work in the remaining months of 2011 will be directed at resolving the relationship between  $\delta^{15}\text{N}$ , N, and diatom community change in the sediment record and resolution of the potential impact of diagenesis in influencing the sediment  $\delta^{15}\text{N}$  signature. We plan to use a stepped approach; 1) Using sediment surface concentrations, a maximum impact of diagenesis will be calculated, 2) Three sedimentation traps were retrieved from Whitebark Moraine Pond and these will be analyzed to determine the modern, autochthonous  $\delta^{15}\text{N}$  signature, and 3) Diatom community change is highly correlated with  $\delta^{15}\text{N}$ , supporting an



atmospheric source. Further confirmation of the relationships will be completed using multivariate statistical techniques.

Estimation of critical loads for GRTE is dependent on evaluating the role of diagenesis in sediments and will follow by Sarah Spaulding and Jill Baron.

Five macrofossils from the long core from Whitebark Moraine Pond have been submitted for  $^{14}\text{C}$  dating by John Southen, UC Riverside, to provide age chronology. Sediments from the core will inform our interpretation of the millennial scale biological record in relation to the decadal record in GRTE.

Sediment processing and analysis on the Phelps, Bradley, Snake River Oxbow, and long core from Whitebark Moraine Pond are in progress at INSTAAR. The sediment records, particularly from Phelps and Bradley lakes, will allow us to determine if lower elevation, forested watersheds respond to deposition of  $\delta^{15}\text{N}$  in the same manner as high elevation sites. We think analysis of these cores will further clarify the regional atmospheric deposition impacts, however, they were not included in our proposal budgets and are currently only partially funded.

Quantitative metals analysis of sediments for Pb, Hg (ICPMS). Consider other elemental analyses, including P, As, Ti, Fe, Mn, Mg, K- estimated cost for processing is 60-100 samples per hour at a cost of \$100/hour and will be covered by Jill Baron.

We have not yet determined if we will run sediment pigment analysis at INSTAAR using HPLC. Costs would be minimal, but would require technician time. Not budgeted.

The 30 year old microscope at INSTAAR has developed problems in the stage and focussing mechanisms. The microscope has been repaired, but should be replaced in the near future. Spaulding is working to obtain \$30K for replacement, but a funding source not yet determined.