

**DEVELOPMENT OF MONITORING PROTOCOLS FOR NITROGEN & SULFUR
SENSITIVE BOG ECOSYSTEMS**

WBEA SUMMARY REPORT JANUARY 2013

Principal Investigators: Drs. Melanie A. Vile & R. Kelman Wieder, Villanova University
Dr. Shanti Berryman, Integral Ecology Group & Dr. Dale Vitt, University of Southern Illinois

Peatlands are a prevalent landscape feature in the boreal regions of Alberta, Canada, and represent large reservoirs of sequestered carbon (C) and nitrogen (N). Cycling of C and N in peatlands is intrinsically linked, and this is especially the case in bogs, peatlands that are isolated from both ground- and surface-water inputs, and receive nutrients exclusively from the atmosphere, which in the absence of pollution, maintain N-limited, nutrient-poor ecosystems. One growing concern associated with the development of Alberta's Oil Sands (AOS) is the potential for regionally elevated deposition of N(NO_x) and S (SO_y) compounds to impact sensitive bog ecosystems. Prior to AOS development, N inputs to bogs were limited exclusively to (1) biological N fixation, and (2) bulk atmospheric deposition. Our goals are to determine if there is an impact of N and S deposition on sensitive bog vegetation by establishing a network of sites spanning varying distances from the heart of the oil sands mining region and to develop a monitoring protocol for assessing N and S deposition based largely on bogvegetation. We seek to ask the following two questions: 1) are bogs important early warning indicators of pollution, and 2) if yes, what should we measure?

In this progress report, after 4 field seasons of data collection, we provide a summary of results to date, substantive trends, and initial recommendations.

Atmospheric Deposition

Using ion exchange resin collectors, we have documented patterns of decreasing NO_3^- -N, total dissolved inorganic N (DIN: NO_3^- -N+ NH_4^+ -N), and SO_4^{2-} -S, deposition with increasing distance from the oil sands mining area; for each analyte, deposition was much lower at our control site (Utikuma) than at the sites within 75 km of the nearest mine (Table 1). We also have documented that Ca^{2+} and Mg^{2+} deposition decreases dramatically with increasing distance from the nearest mine (data not shown; analysis of resin extracts has been completed for 4 of the 7 collections). We had placed resin collectors in the open and beneath black spruce canopies. Overall, NH_4^+ -N deposition was higher in the open than in throughfall, NO_3^- -N deposition was similar in the open and in throughfall, and SO_4^{2-} -S deposition was higher in throughfall than in the open. Detailed analysis will be provided in the final report.

Table 1. Mean deposition of N and S from ion exchange resin collectors; values are weighted (by the number of days that collectors were in place in the field) daily mean deposition \pm standard errors, converted to annual values.

Site	Distance to closest mine site (km)	Deposition (kg/ha/yr)			
		NH_4^+ -N	NO_3^- -N	DIN	SO_4^{2-} -S
JPH4	14	0.81 \pm 0.18	0.92 \pm 0.13	1.76 \pm 0.27	24.8 \pm 4.7
Mildred	16	0.58 \pm 0.05	1.52 \pm 0.16	2.11 \pm 0.19	22.0 \pm 2.4
McKay	21	0.55 \pm 0.05	1.01 \pm 0.11	1.56 \pm 0.14	19.1 \pm 2.9
McMurray	53	1.02 \pm 0.20	0.87 \pm 0.09	1.86 \pm 0.23	12.8 \pm 1.4
Anzac	73	0.57 \pm 0.06	0.85 \pm 0.07	1.42 \pm 0.09	11.8 \pm 1.1
Utikuma	249	0.30 \pm 0.03	0.36 \pm 0.04	0.66 \pm 0.05	4.3 \pm 0.4

Weather Station Data

We have had a WatchDog® weather station at each of the WBEA sites, recording hourly measurements of air temperature, precipitation, relative humidity, wind speed, and wind direction. Detailed analysis of the weather station data will be provided in the final report.

Biological N₂ fixation as an input of N

Tatjana Prša completed her M.S. degree under Dr. Vile's supervision in 2011. Her research quantified biological N₂ fixation across our WBEA sites. Rates of biological N₂ fixation differed between moss species. Using percent cover of moss species at each of our sites, we have shown that biological N₂ fixation can provide N inputs to bogs ranging from 4 to 14 kg/ha/yr, and that enhanced N deposition provides a negative feedback on this process, thereby decreasing the importance of this biological input. This work is complete. Detailed analysis will be provided in the final report. A manuscript is in preparation, and hopes to be submitted within the next couple of months (March 2013).

Sphagnum fuscum Net Primary Production

Under the prevailing belief that bogs of continental western Canada are nitrogen limited, we had thought that *Sphagnum fuscum* growth in length (cm/yr) and net primary production (g/m²/yr) would be stimulated with increasing atmospheric N deposition. We found a weak pattern of increased growth in length with increasing proximity to a mine site, but no clear pattern with net primary production. Our initial expectation that *Sphagnum fuscum* growth would provide an excellent monitor of N deposition has not been substantiated. Remaining work to be done is to process samples for near-surface bulk density of *S. fuscum* peat, to convert the 2012 growth in length data to net primary production data. Detailed analysis will be provided in the final report.

Bog Plant Tissue Chemistry

Over the four field seasons, we have collected nearly 8000 samples (12 plant species, 5 plots per site, 6 sites, 5-7 collection dates between May and October each year) for analysis of C, N, and S, as well as $\delta^{15}\text{N}$ (through 2011 only).

Ombrotrophic bogs can serve as early warning indicator of pollution if monitoring protocols focus on the most sensitive plant species, in particular, mosses and lichens. Specifically, the tree lichen, *Evernia mesomorpha*, offers the greatest potential as a monitoring tool to assess the spread of elevated atmospheric N and S deposition from oil sands development by exhibiting several patterns: with increasing distance from the nearest mine (a) there is a distinct natural abundance ¹⁵N signature that becomes isotopically more negative, and this pattern is most pronounced in *Evernia mesomorpha* (b), tissue N and S concentrations decrease, and (c) the visual quality of the lichen community and of *Evernia mesomorpha* especially (smaller size, less robust, and less abundant) degrades. *Sphagnum fuscum* and *Oxycoccus microcarpus* (cranberry) clearly show a response to sulfur and carbon concentrations along this same gradient. Moreover, regression analysis of N and S concentrations in several species has revealed that N, and to a lesser extent S, concentrations in plant tissues have been steadily increasing over the past four years. We have completed analyses on about 75% of the collected samples. We have begun to identify aspects of plant tissue chemistry in several species that could be used as monitors of the spread of N and S deposition across the oil sands region. Detailed analysis will be provided in the final report.

Bog Pore Water Chemistry

At each site, we installed 3 pore-water samplers allowing us to collect bog pore water as a function of depth (1-100 cm, with sampling at every 10 cm depth interval; approximately 3000 samples over 4 field seasons). Samples are analyzed for pH, conductivity, NH_4^+ -N, NO_3^- -N, SO_4^{2-} -S, total dissolved C, dissolved organic C, total dissolved N and dissolved organic N. We had anticipated seeing increases in dissolved N and S species at the top of the water table with increasing N and S deposition (increasing proximity to a mine). This expected pattern has not been substantiated. However, we have documented a pattern of the DOC/DON (dissolved organic carbon/dissolved organic nitrogen) ratio in peat porewater ranging from about 15 at sites closest to a mine to over 50 at sites furthest away from a mine. Bog water chemistry may provide another approach to monitoring. Analyses on these samples are 95% complete. Detailed analysis will be provided in the final report.

Accumulation of C, N, and S in Peat

We collected 5-7 peat cores, 50-80 cm deep, from each site, sectioned each core into 3-cm depth increments, acid digested each depth increment to extract ^{210}Pb , quantified the ^{210}Pb activity by α spectroscopy, and calculated the age of each depth increment using the constant rate of supply of ^{210}Pb model. Each depth increment also is analyzed for bulk density as well as C, N, and S concentrations, allowing us to quantify the total amount of C, N, or S accumulated in the growing peat deposit (units of kg/ha/yr) over the past 0-25 or 25-50 year time horizons. Results show that for the WBEA sites, C, N, and S accumulation over the past 25 years increases with increasing proximity to a mine site, but accumulation is similar across all sites for the 25-50 year time horizon. Thus, oil sands development has increased accumulation of C, N, and S in peat. Analyses of the WBEA peat cores are nearly complete; 9 cores still need to be analyzed for S concentrations. Detailed analysis will be provided in the final report.

Decomposition of Standard Materials

At each site, we have placed 15 pure cellulose (filter paper) and 15 birch sticks (tongue depressors) decomposition bags, deploying a total of 375 bags of each material. Five replicate bags have been collected each year and have been analyzed for mass loss, and concentrations of C, N, and S. We anticipated a pattern of increasing decomposition with increasing N deposition. This pattern has been observed for the cellulose, but not the birch stick, bags. Decomposition rates (mass loss) has been well correlated with the accumulation of N and S in the remaining cellulose and birch stick materials. These results suggest that across the oil sands region, cellulose decomposition rates may provide a tool for monitoring N and S deposition. Decomposition bags collected in 2012 still need to be analyzed. Detailed analysis will be provided in the final report.

Lichen Transplant Study

In 2009, lichens (*Evernia mesomorpha*) collected from our control site (Utikuma) were tied to branches and placed in black spruce trees at all of our WBEA sites (3 black spruce trees, 3 branches per tree per site). One lichen branch was collected from each tree in 2010 and 2012. Collected samples were analyzed for chlorophyll *a*, chlorophyll *b*, and phaeophytin *a* concentrations, as well as total C, N and S concentrations. These samples demonstrated an increase in chlorophyll *a* and a decrease in phaeophytin with increasing proximity to the OSMR. Samples from the 2012 collection (which were transplanted for three years total) are still being analyzed. Transplantation of healthy lichens from sites distant from the

oil sands region to sites within the oil sands region may provide a useful monitoring tool. Detailed analysis will be provided in the final report.