

FINAL REPORT

High-frequency Analysis of Stream Chemistry to Establish
Elemental Cycling Regimes of High-latitude Catchments

SERDP Project RC-2507

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14. ABSTRACT The objectives of this Limited Scope project were to evaluate the performance of instream sensors measuring solute concentrations in high-latitude streams and to assess the relevance of high-frequency records of stream chemistry for studying ecosystem responses to disturbance. Sensors measuring nitrate, fluorescent dissolved organic matter, temperature, turbidity, conductivity, and optical properties of organic matter were deployed in two streams draining the US Army's Yukon Training Area. Laboratory tests were performed to evaluate the response of sensor output to temperature, turbidity, and colored dissolved organic matter. Technical considerations and improvements for implementing instream sensors as part of an environmental monitoring program include permanent mounting of sensors to existing infrastructure and specifically for high-latitude streams with high concentrations of colored dissolved organic matter, further research into the relationship of the concentration of dissolved organic matter with its chemical composition and optical properties. Use of instream sensors for monitoring water chemistry is feasible in high-latitude, boreal streams and near real-time monitoring of solute chemistry could assist in the land stewardship mission of the military to inform the timing and conditions under which training activities would yield minimal effects on water quality.					
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Figure 10. Wavelet coherence plots depicting correlation of fDOM concentration and stream temperature for French (top) and Moose (bottom). The color ramp illustrates the correlation coefficient, with warm colors indicating a strong association between the two attributes. Left-pointing arrows indicate negative correlation and right-pointing arrows indicate positive correlation. Upward arrows indicate that temperature peaks lead fDOM peaks, whereas downward arrows indicate the opposite.

List of Acronyms

DOC dissolved organic carbon

EXO multi-parameter sonde manufactured by Yellow Springs Inc.

fDOM fluorescent dissolved organic matter

NO₃⁻ nitrate

SUNA Specific Ultra-Violet Nitrate Analyzer manufactured by Satlantic, Inc.

Keywords

Alaska
dissolved organic carbon
dissolved organic matter
fire
nitrogen
nitrate
permafrost
sensors
streams

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Abstract

Objective: The objectives of this Limited Scope project were to evaluate the performance of instream sensors measuring solute concentrations in high-latitude streams and to assess the relevance of high-frequency records of stream chemistry for studying ecosystem responses to disturbance. High-latitude ecosystems are subject to disturbance by fire and permafrost thaw. Data describing material outputs from catchments could indicate the duration over which ecosystems are responding to disturbance, thereby indicating when military-owned lands may be most sensitive to training activities. This was a “high-risk” project because instream sensors have not been applied broadly in high-latitude streams. High-latitude streams are characterized by sharp changes in water temperature and by colored dissolved organic matter, both of which can interfere with the signals measured by optical sensors. Research was therefore designed to deploy and test the performance of sensors measuring dissolved organic matter and nitrate in boreal streams.

Technical approach: Commercially available sensors measuring nitrate, fluorescent dissolved organic matter, temperature, turbidity, conductivity, and optical properties of organic matter were deployed in two streams draining the US Army’s Yukon Training Area. Data were collected by sensors every 15 minutes, and autosamplers collected less frequent grab samples for calibration of sensor output. One stream drained lowland boreal forest that had not burned in more than ~75 years, and a second stream drained a catchment partially burned two years prior to the research.

Laboratory tests were performed to evaluate the response of sensor output to temperature, turbidity, and colored dissolved organic matter. High-frequency data were analyzed using wavelets, a spectral method for describing the temporal scales of variation. Indicators of impending regime shifts were also calculated to compare the stability of biogeochemical cycles in the recently burned and unburned catchments.

Results: High-frequency data collected by sensors revealed temporal patterns that are not captured by lower-frequency monitoring programs. Importantly, large fluxes of nitrate and dissolved organic matter occurred during storms, and these would be missed by sampling programs conducted using grab samples. Second, diurnal fluctuations were apparent in both nitrate and dissolved organic matter, which may ultimately be useful in understanding the relative contributions of biology and hydrology to the biogeochemical cycles of catchments. Temporal patterns in all solutes measured by sensors were remarkably similar between the burned and unburned catchments, which might indicate resilience of lowland catchments to fire.

This Limited Scope project also indicates several technical considerations and improvements for implementing instream sensors as part of an environmental monitoring program. First, due to the brief duration of this project, sensors were installed on the streambed, and this introduced several limitations on data quality that would be eliminated by permanent mounting of sensors to existing infrastructure. Second, in boreal streams, which carry high concentrations of colored dissolved organic matter, fluorescent dissolved organic matter cannot provide an index of dissolved organic carbon concentration across the full range of concentrations observed, due to the changing chemical composition of organic matter at the scales of both individual storms and across seasons. Future research that probed the nature of

composition vs. concentration relationships could yield reliable calibration relationships between fDOM and dissolved organic carbon.

Benefits: Use of instream sensors for monitoring water chemistry is feasible in high-latitude, boreal streams. Sensors could be installed across a network of sites to capture unpredictable changes, such as those resulting from fire and climate regimes. Alternatively, installation at a particular location downstream of training activities or infrastructure could provide near real-time monitoring of the effects of activities occurring within the catchment on water quality. A nitrate sensor would be particularly useful for capturing effects of training activities involving nitrate-based explosives on downstream water quality.

Objective

The primary objective of this Limited Scope project was to evaluate the performance of instream sensors measuring solute concentrations in high-latitude streams. Although the technology of optical sensors for detecting water-quality parameters has rapidly improved, and deployment of sensors has recently increased in a diversity of environmental settings, there have been few deployments in high-latitude streams. Streams draining boreal forest may pose challenges to implementation of optical sensors due to potential for temperature fluctuations and presence of dark water color, which limits the transmissivity of light and constrains the efficacy of optical measurements. A secondary objective was to assess the relevance of high-frequency records of stream chemistry for studying ecosystem responses to disturbance.

This project focused on demonstrating proof-of-concept regarding collection of accurate water-quality data from boreal streams using optical sensors, and development of appropriate calibration relationships for correcting for the interfering effects of temperature, water color, and suspended sediments. An additional objective was to apply statistical methods for analysis of time series to describe patterns in water-quality data, and in particular to use these methods for detection of the effects of disturbance on the solute chemistry of boreal streams. The criteria for success were therefore: 1) successful collection of accurate, high-frequency water chemistry data from two boreal streams, and 2) application of statistical methods for time series to the resulting data.

Meeting these objectives would reduce risk in developing a Standard Proposal aimed at evaluating high-frequency records of stream chemistry as a tool for predicting and detecting regime shifts, as envisioned in the SERDP Statement of Need. Successful collection of data by the sensors tested in this proposal would demonstrate the efficacy of investment in further sensors to allow expansion to a network of sites varying in disturbance history necessary to test theory relating elemental cycles and disturbance of high-latitude ecosystems caused by climate change.

Background

Environmental issues

Climate, ecosystem structure, and disturbance interactively influence elemental cycles of high-latitude catchments. Low mean annual temperature results in slow rates of decomposition, and accumulation of large stores of organic matter in soils [Van Cleve *et al.*, 1991]. This organic matter is also subject to leaching losses, and as a result, high concentration of dissolved organic matter (DOM) characterizes high-latitude streams [O'Donnell *et al.*, 2012a; Wickland *et al.*, 2007]. Primary productivity of terrestrial ecosystems of the boreal forest is typically limited by nitrogen (N), resulting in high rates of internal recycling of N [Kielland *et al.*, 2007; Van Cleve *et al.*, 1991] and limiting loss to aquatic ecosystems. However, streams draining deciduous-dominated catchments with low extent of permafrost have higher concentration of inorganic N and lower concentration of DOC than catchments underlain by permafrost and containing extensive stands of black spruce [Balcarczyk *et al.*, 2009; Jones *et al.*, 2005; Petrone *et al.*, 2006]. These patterns are hypothesized to result from increasing depth of flowpaths that drain catchments as permafrost degrades. Deeper flowpaths are routed through mineral-rich soils that may support lower rates of plant and microbial retention of inorganic N compared to shallow soils [Harms and Jones, 2012].

Fire is the dominant disturbance in the boreal forest, initiating predictable successional sequences and altering biogeochemical cycles across broad spatial extents. Loss of C from ecosystems due to combustion during fires causes reduced hydrologic flux of DOC, whereas NO_3^- concentration can increase in streams following fire [Betts and Jones, 2009]. These are typical responses of biogeochemical cycles to fire in forest ecosystems [Bayley et al., 1992; Williams and Melack, 1997]. Increased fluxes of nutrients following fire may occur due to increased microbial decomposition [Wan et al., 2001], changes in the chemical and physical structure of soils [O'Donnell et al., 2012b], or due to increased thaw depth [Jorgenson et al., 2010].

Disturbance regimes may be accelerating in Interior Alaska, with unpredictable consequences for ecosystem processes. Climate change in Alaska has resulted in increased mean annual temperature (2-3°C from 1954-2003) and warming at high latitudes has proceeded at twice the rate of lower latitudes [ACIA, 2005]. Precipitation has also increased, and climate models project increased precipitation as snow, a longer snow-free season, and increased frequency of extreme precipitation events [ACIA, 2005; Serreze et al., 2000]. Changes in climate have coincided with decreased areal extent of permafrost and an increase in active layer depths (soils above permafrost that freeze and thaw annually) [Yoshikawa and Hinzman, 2003; Yoshikawa et al., 2002].

The fire regime of northern high-latitudes has also intensified, shifting toward more severe fires (defined by increased depth of burning), and an increase in the size of fires that has contributed to a doubling in the annual areal extent burned over the past 40 years [Balshi et al., 2009; Flannigan et al., 2005; Kasischke et al., 2010]. These changes are attributed to increased fire later in the growing season caused by elevated summer temperatures [Johnstone et al., 2010; Kasischke et al., 2010; Turetsky et al., 2011].

Rapid changes in the dynamics of permafrost and fire have significant consequences for the structure and function of ecosystems at northern high-latitudes. Inorganic N availability increases following experimental warming of soils and is subject to leaching, whereas C is released as CO_2 [Allison and Treseder, 2008; Mack et al., 2004; Natali et al., 2011; Schimel et al., 2004; Schuur et al., 2007]. Increased gaseous flux of C in response to warming may reduce the load of DOM transported to streams [Striegl et al., 2005], although this mechanism remains untested. Recently thawed permafrost may release previously stored inorganic nutrients, which are then subject to leaching [Keuper et al., 2012]. Rapid loss of permafrost that initiates formation of thermokarst features can mobilize inorganic N from cryoturbated soils [Abbott et al., 2015; Bowden et al., 2008; Harms et al., 2014], resulting in spatially isolated, but acute increases in nutrient concentration.

Simultaneous acceleration in multiple aspects of the disturbance regime may generate previously undocumented ecosystem states, and as a consequence, there is great uncertainty in predicting ecosystem processes such as elemental cycling under future scenarios for the boreal forest (Chapin et al. 2010). Catchment-integrated signals in nitrate and DOM export could be used to indicate the response of C and N cycling to changes in climate, fire, and permafrost regimes. Specifically, high-frequency records collected by instream sensors provide the data needed to characterize patterns at multiple temporal scales [Kirchner and Neal, 2013; Rode et al., 2016] and to support estimates of indicators of impending regime shifts, which require long-term records that adequately capture the important time scales of variation in an ecosystem [Batt et al., 2013; Carpenter et al., 2011].

Technical issues

Although instream sensors hold promise for generating the high-frequency data needed to detect and potentially predict changes in ecological states, several technical issues require consideration before widespread deployment in boreal streams. First, wide seasonal variation in water temperature and sharp diurnal changes in temperature that are characteristic of high-latitude streams could influence accuracy of measurements. Second, DOM, and particularly colored DOM, can interfere with detection of solutes by optical methods, because DOM dampens transmission of UV light and therefore the resulting measured signals [Downing *et al.*, 2012; Pellerin *et al.*, 2013]. This is a potential analytical barrier to using optical methods to measure NO_3^- and DOM in high-latitude streams, which often have high concentration of colored DOM. Finally, strong correlation between fDOM and DOC concentrations in some watersheds [Wilson *et al.*, 2013], particularly those lacking high loads of suspended sediments, allows modeling of DOC fluxes based on fDOM. Use of these relationships in headwater streams of the boreal forest is promising as these streams typically have low suspended sediment loads, but local relationships between fDOM and DOC concentration must be constructed at each site to determine whether fDOM can be used as a surrogate for carbon [Saraceno *et al.*, 2009].

Materials and Methods

Study sites

Sensors were deployed in two streams, French Creek and Moose Creek, which drain the Yukon Training Area, managed by the US Army (Fig. 1) near Fairbanks, AK. Sites were chosen for ease

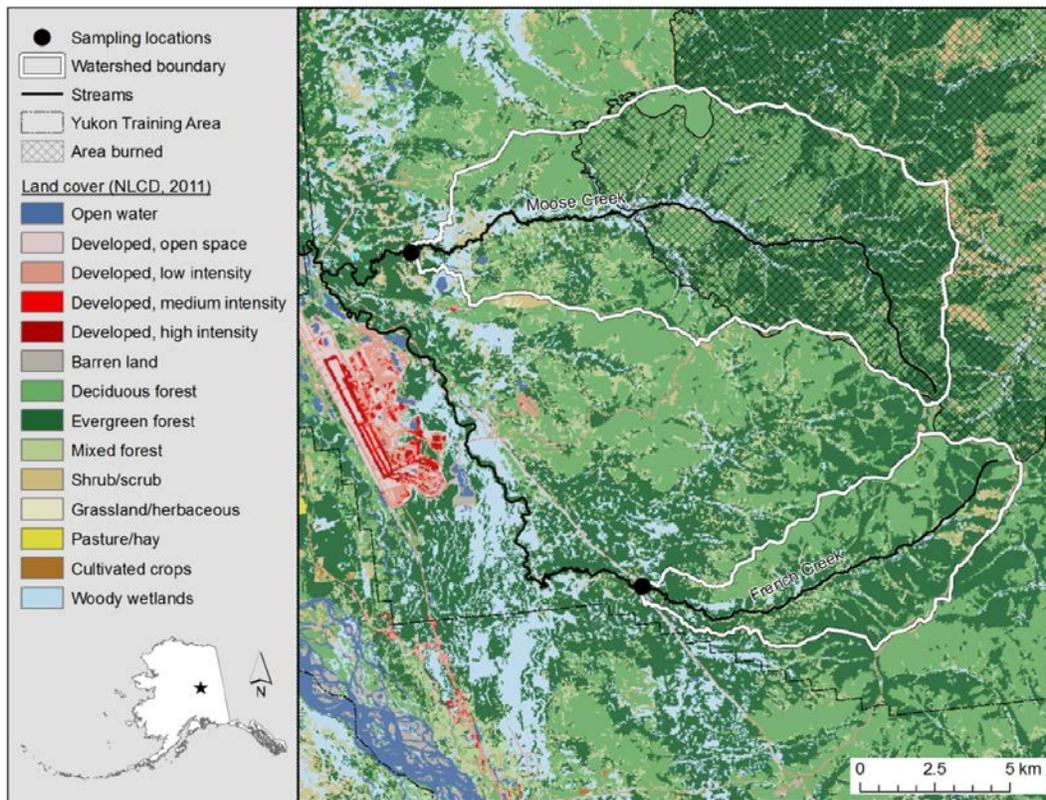


Fig. 1. Map of study sites within the Yukon Training Area depicting contributing areas at the point of sensor installation, land use, and the area burned by the 2013 Stuart Creek Fire.



Fig. 2. Sites of sensor installation at French Creek (top) and Moose Creek (bottom). Note ice lining the channel of Moose Creek.

equipped with multiple sensors. The SUNA measures nitrate concentration and additionally reports absorbance of light at 254 nm (a_{254}), an indicator of the aromaticity of dissolved organic carbon. Two measurements were collected every 15 min. Power for the SUNA was delivered via an 80 Ah battery connected to a 20W solar panel. The EXO was equipped with sensors for fluorescent dissolved organic matter (excitation: 365 nm, emission: 480 nm), turbidity, conductivity, and temperature. These parameters were measured once every 15 min. The EXO was powered by onboard 6V batteries. Both sondes included integrated wipers that cleaned the read windows of optical sensors before each set of measurements (i.e., once every 15 min).

Sondes were attached to a custom-built concrete platform placed on the streambed (Fig. 2). The EXO sondes were deployed vertically, within a protective housing of PVC. SUNAs were deployed horizontally, with a perforated shield at the upstream end of the sonde. Deployment of sondes via this platform was necessitated by the short duration of the project, but it did have consequences for the quality and continuity of data collection. First, placement of sensors near the streambed resulted in greater interference by sediment than would occur if sensors were suspended higher in the water column. Second, significant distance between the stream and the power source, which was positioned above flood level on the bank, resulted in occasional disconnection of extended power cables by wildlife. Third, sensors were inaccessible for servicing during flood conditions. Fourth, we were unable to continuously gauge stream discharge using pressure transducers, because of melting of bedfast ice at the beginning of the

of accessibility, to allow weekly checks of equipment. Permission for site access was granted by Eielson Air Force Base, Fort Wainwright Natural Resources, and Alyeska Pipeline. Both streams drain catchments typical of the Yukon-Tanana Uplands, vegetated by balsam poplar (*Populus balsamifera*) and Alaskan paper birch (*Betula neoalaskana*) on south-facing slopes and black spruce (*Picea mariana*) on north-facing slopes. At the site of sensor installation, French Creek drains a 44 km² catchment that has not burned in over 75 years. Moose Creek drains 112 km² at the point of sensor installation, and ~50% of the catchment burned in the Stuart Creek Fire of 2013. Ideally, sensors would have been installed on Moose Creek within the burn perimeter, but as this is an active military training site, the stream could not be accessed further upstream.

Field deployments of sensors and sampling equipment

At each site, we installed two sondes: a Specific Ultra-Violet Nitrate Analyzer (SUNA V2; Satlantic) and an EXO (YSI)

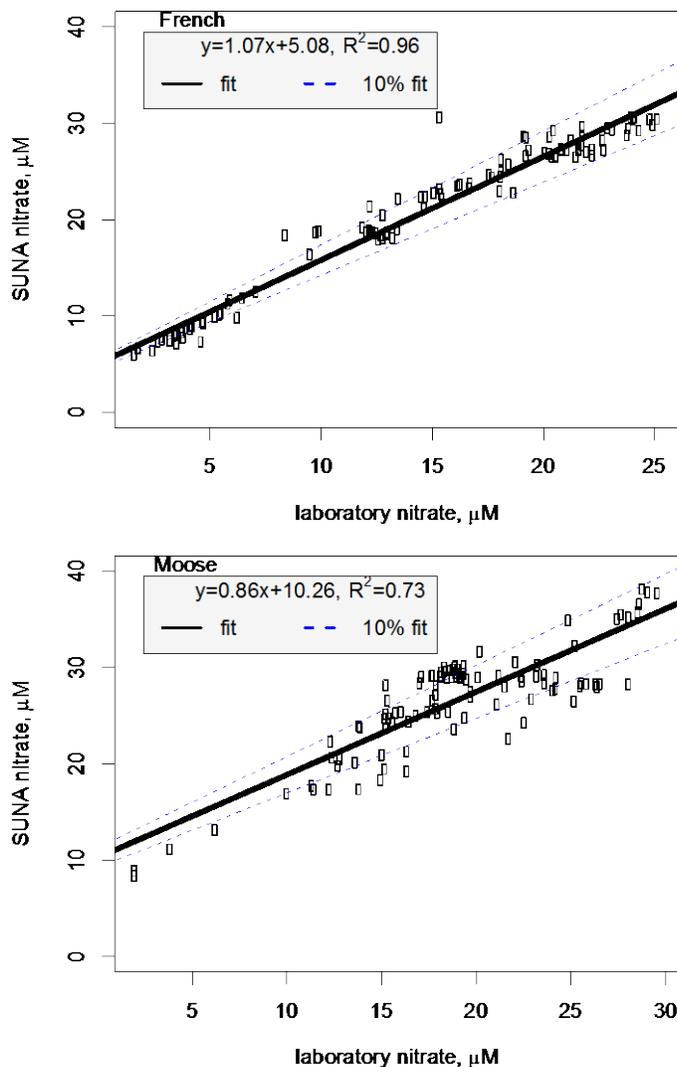


Fig. 3. Calibration relationships for nitrate concentration measured on grab samples in the laboratory and by the SUNA in the stream. Black lines indicate the regression relationship. Blue dashed lines indicate values $\pm 10\%$ of the predicted relationship, the expected precision of the measurements specified by the manufacturer.

were calibrated to laboratory-measured values from the daily and storm-based grab samples collected by the autosampler. Nitrate in grab samples was measured by ion chromatography (Dionex ICS-2100, AS-18 columns). Calibration relationships for nitrate largely met the manufacturer's specifications for French Creek, but were more variable for the sensor deployed at Moose Creek (Fig. 3). The positioning of the sensor near the streambed resulted in occasional clogging of the sensor read window with sediment and inaccessibility of submerged sensors during high flow conditions limited opportunities for sensor maintenance during these times.

measurement period and streambed movement throughout the period of deployment. All of these issues can be remedied by attachment of sensors to infrastructure, but this requires permission of the owners of the infrastructure. We have successfully employed such an approach in subsequent projects in other regions. The two sites studied here were chosen for their accessibility at road crossings, and sensors and power sources could be attached to these bridges in future deployments.

For calibration purposes, grab samples were collected daily, and every 2 hours during storms. Samples were collected by autosamplers (ISCO) configured to collect one sample at 20:00 daily. Autosamplers were configured with a tipping bucket rain gauge (0.254 mm limit of detection) and programmed to commence sampling every 2 hours following precipitation intensity exceeding 0.76 mm/h. Eight samples were allocated to daily samples, and the remaining 16 to storm samples. Samples were retrieved weekly, filtered to 0.7 μm (Whatman GF/F) in the laboratory, and frozen until analysis.

Sensor calibration

SUNAs were calibrated in Nanopure water ($>18 \text{ M}\Omega$) following the manufacturer's instructions. Calibration measurements prior to and following deployment were within -2 to $+2 \mu\text{M}$ nitrate. Sensor-determined nitrate values

Sensors for fDOM, conductivity, and turbidity were calibrated in the laboratory prior to sensor deployment following manufacturer instructions, using certified standards. Additional calibrations of the fDOM sensor were performed following sensor deployment. These included calibrations needed to correct fDOM measures for temperature, turbidity, and extinction of the signal by colored dissolved organic matter. Previous research [Downing et al., 2012; Watras et al., 2011] has indicated that the correction factors for fDOM are sensor-specific, and separate calibration relationships were thus developed for each sensor.

The fluorescence signal is altered by temperature, introducing bias into field-measured fDOM. Temperature corrections to fDOM measurements were performed following Watras et al. 2011. Sensors were set to log every minute and placed in stream water that was cooled by an ice bath. Ambient temperature was then warmed to 30°C in an incubator. The resulting relationship between temperature and fDOM was used to correct fDOM measurements to a reference temperature of 20°C by:

$$fDOM_t = fDOM_m / [1 + \alpha(T_m - T_t)],$$

where α is the ratio of the slope and intercept of the temperature-fDOM

relationship, T is temperature, r represents the reference temperature (here, 20°C), and t represents the stream temperature at the time of fDOM measurement. Satlantic, the manufacturer of the SUNA V2, indicates that temperature sensitivity does not affect output of the nitrate sensor.

Concentration of fDOM was additionally corrected for turbidity, which reduces the transmission of the UV light used to measure fDOM. We performed experiments in the laboratory to determine the extinction of the fDOM signal due to suspended particles. Soil was added to stream water to slowly increase turbidity while the fDOM and turbidity sensors recorded values every minute. A regression function between turbidity and fDOM was estimated

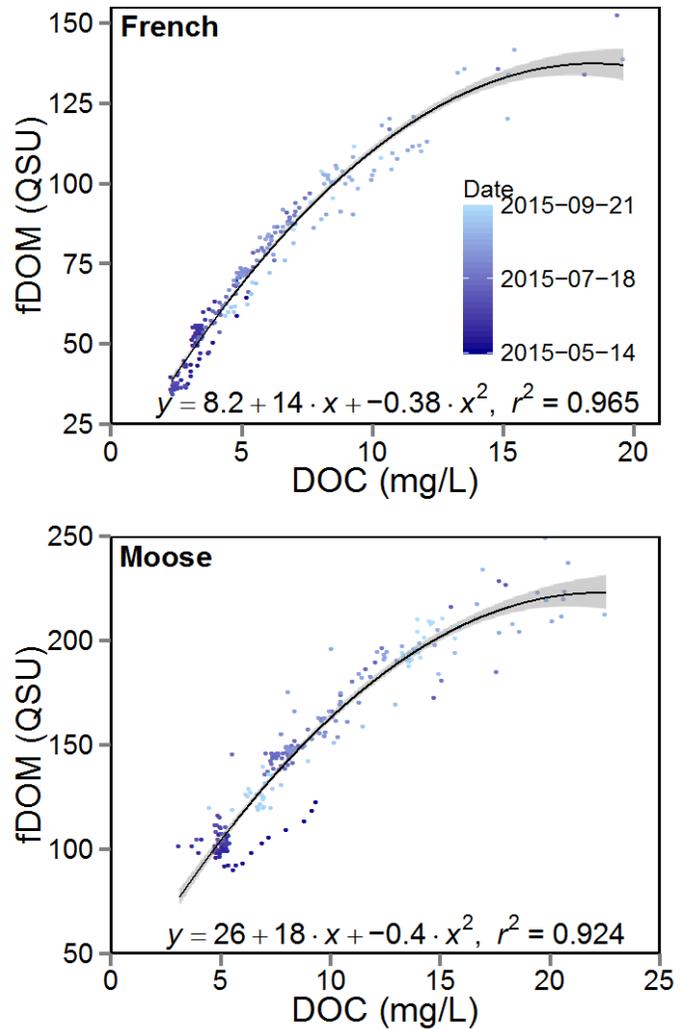


Fig. 4. Calibration of relationship of fDOM, measured in situ, and DOC concentration measured on grab samples in the laboratory. The 95% confidence band for the relationship is shown in gray. Color of points corresponds to the sampling date.

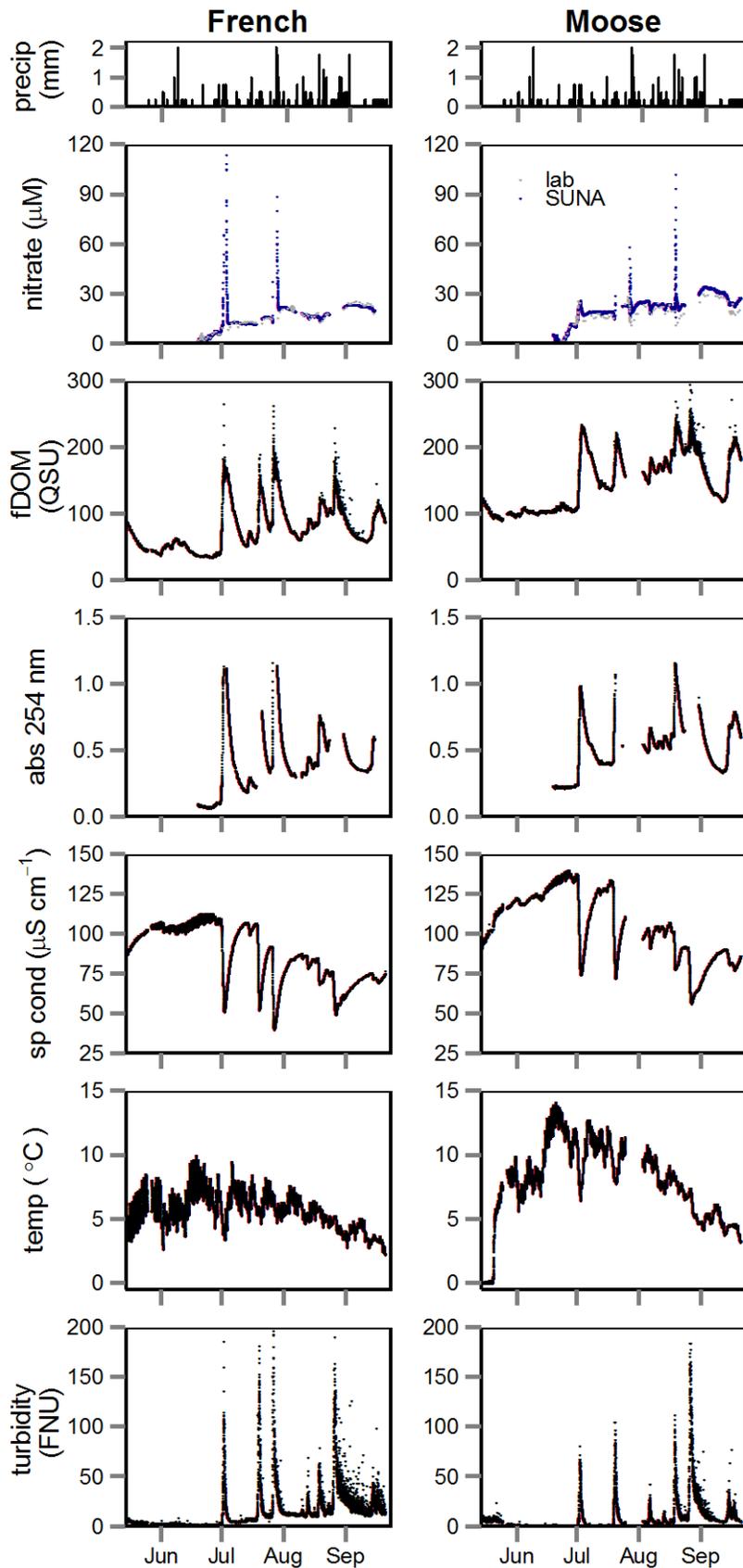


Fig. 5. Time series of parameters monitored using instream sensors at French and Moose Creeks.

from the linear portion of the resulting curve, and applied to the measured fDOM values using the simultaneous turbidity measurements collected by the sonde.

We explored the relationship between colored DOM, which reduces transmission of light, and values of fDOM measured by the sonde in attempt to develop a correction factor associated with colored DOM. In the laboratory, colored DOM was slowly added to stream water while the EXO logged fDOM every minute. Discrete samples of the resulting solution were collected and the absorbance at 254 nm (a_{254}) was measured on a spectrophotometer. A regression function was estimated based on the linear portion of the relationship of a_{254} and fDOM. However, we did not apply this relationship to correct fDOM measures for interference by colored DOM, because the slope of the relationship of a_{254} and fDOM measured in situ varied significantly through time. Thus, the concentrations of fDOM presented here likely underestimate the true concentrations in the streams.

Fluorescent dissolved organic matter represents an unknown fraction of the total pool of dissolved organic matter. For purposes of ecosystem carbon budgets, it would be advantageous to develop a calibration

relationship between fDOM and dissolved organic carbon concentration. We attempted to calibrate measures of fDOM to dissolved organic carbon concentration measured in the laboratory (non-dispersive infrared gas analysis, Shimadzu TOC-L) on grab samples collected by the autosamplers. The manufacturer of the fDOM sensor reports that relationships between fDOM and DOC are sub-linear, but others have developed linear calibration relationships between fDOM and DOC following correction for temperature and color effects [Wilson *et al.*, 2013] by assuming that composition of DOM is homogeneous within a season. We observed strongly non-linear relationships between fDOM and DOC (Fig. 4), and the relationships are particularly confounded at high concentrations. Changes in the composition of DOM over the course of even single storms, as indicated by a254, and the presence of colored DOM likely contribute to the variable and non-linear nature of this relationship. We therefore do not convert measures of fDOM to DOC. It is possible that more detailed analyses of the composition of fDOM alongside future deployments of the fDOM sensor might contribute to development of an accurate calibration relationship between fDOM and DOC concentrations.

Data handling

All data processing was conducted in the R program. Outliers from all records were removed manually following visualization of the data, using criteria of impossible values, erroneous readings relative to surrounding data points, and in conjunction with records of power supply and turbidity. Outliers constituted less than 10% of the raw observations collected by the sensors. Ideally, detection of outliers would occur via automated routines. Several approaches based on moving windows were attempted, but currently available routines including the median absolute deviation applied to moving windows, are biased by extreme outliers, and not sensitive enough to reliably detect outliers against temporal patterns that contain variation at multiple temporal scales (e.g., storm peaks that interrupt a regular diurnal pattern). Methods for quality assurance that could incorporate information from multiple parameters to identify and classify different types of outliers would represent a significant advance. For example, sensor performance can degrade when battery voltage declines during periods of low temperature. Following removal of outliers, we took the mean of the duplicate nitrate and a254 values that were collected within 5 s of one another.

Statistical analysis

We calculated several metrics associated with temporal variation that have been demonstrated as “leading indicators” of regime change [Carpenter and Brock, 2006; Scheffer *et al.*, 2009] and compared them between the disturbed (Moose) and undisturbed (French) sites. These indicators included skewness, kurtosis, standard deviation, and the AR1 coefficient. These metrics indicate when systems are nearing transitions between alternative stable states because systems undergoing transitions exhibit increased variation as they move rapidly between states, as well as decreased ability to return to baseline conditions following perturbations, which leads to “critical slowing down”. Skewness describes the symmetry of a distribution, and may either increase or decrease preceding a transition between states [Guttal and Jayaprakash, 2008]. Similarly, kurtosis describes the proportion of observations near the tails of a distribution, with an increase in extreme values indicative of an impending regime shift. Finally the auto-regressive coefficient (AR1) measures critical slowing down prior to a regime shift, because it quantifies the correlation of measures between time steps. An increase in AR1 therefore indicates increasing similarity between successive measurements, indicative of slowed return to baseline,

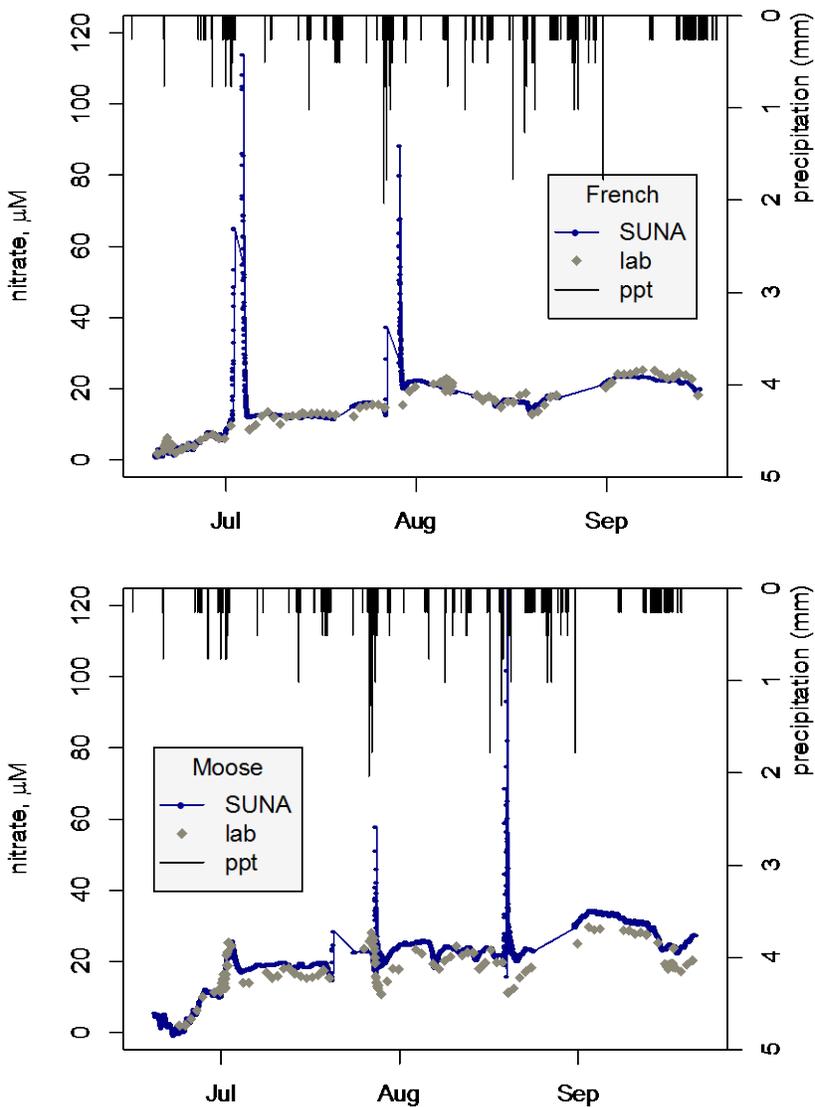


Fig. 6. Detail of temporal patterns in nitrate measured by the sensor and on grab samples analyzed in the laboratory.

Significance of correlation was determined from 1000 Monte Carlo simulations. Results of wavelet analysis are presented visually with further guidelines for interpretation in figure captions. We used the biwavelet package to conduct wavelet analysis.

Results and Discussion

Calibration. Calibration relationships indicated accuracy of field-collected measures of nitrate and fDOM across a wide range of concentrations and varying in situ temperature. For both sites, the slope of the relationship between nitrate concentration measured by the SUNA and in the laboratory was near one, indicating little bias in the values estimated by the SUNA. Details of calibration for both nitrate and fDOM are summarized in the Materials and Methods section.

particularly following perturbations. Standard deviation, skewness, and kurtosis were estimated using functions in base R. AR1 was estimated by fitting a first-order autoregressive, integrated, moving average model (ARIMA) to differenced data in the package forecast. Given the short (15-minute) time steps in these datasets, exploring autocorrelation at longer time lags and over moving windows would be a component of future research.

Wavelet analysis was applied to summarize the time scales of variation in nitrate and fDOM measured by the sensors. Wavelets decompose a composite signal (here, the time series of nitrate and fDOM) into component signals of distinct frequency, amplitude, and phase, and account for non-stationarity. We also estimated correlation of water temperature with nitrate and fDOM concentrations at multiple temporal scales using wavelet coherence.

Measurement accuracy could be improved through attachment of sensors to permanent

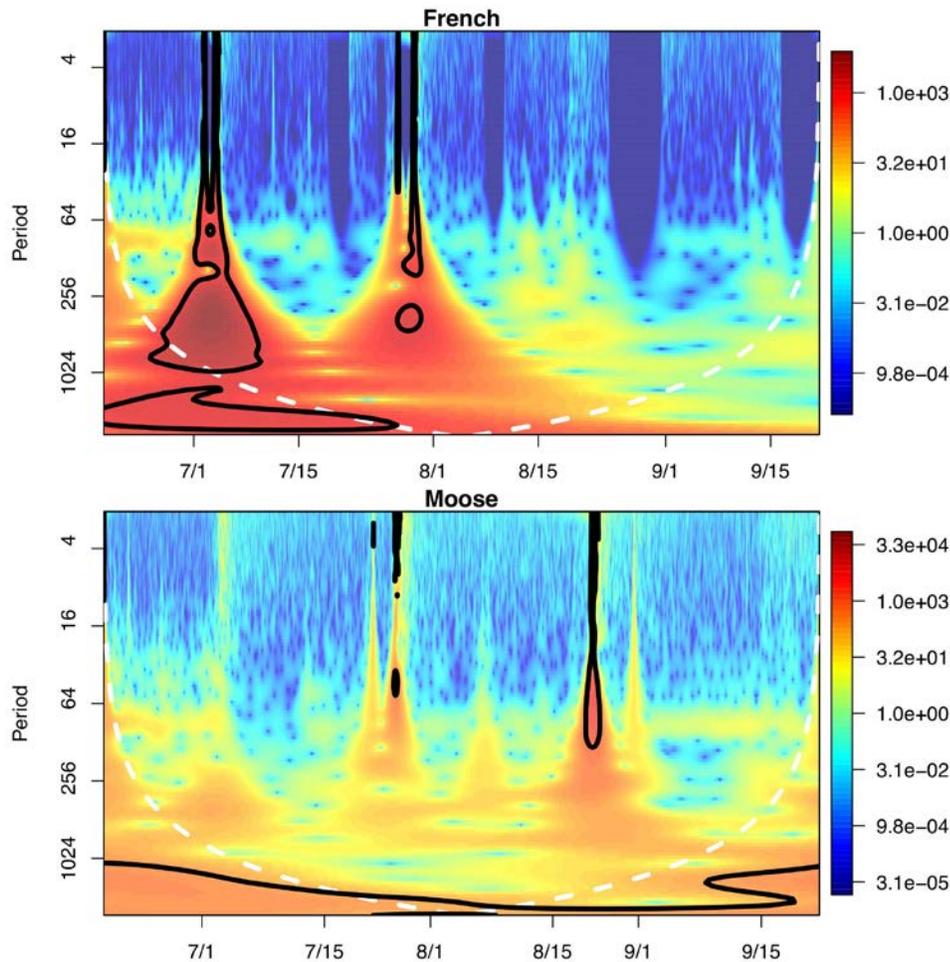


Fig. 7. Wavelet transform of nitrate concentration. Data were collected at 15-minute intervals; periods labeled on the y-axis correspond to 1 h, 4 h, 16 h, 64 h (~3 d), and 256 h (~11 d). Color depicts the wavelet power, or squared amplitude of oscillation, in units of μM^2 , with warmer colors depicting wider temporal variation. Bold black lines outline variance that exceeds the expected value from an auto-regressive (red noise) spectrum. The white line indicates the cone of influence, outside of which edge effects introduce bias into the calculated power.

infrastructure, such as bridges or culverts. Because of the short-term duration of this Limited Scope project, sensors were deployed via removable platforms that rested on the streambed. Based on previous work in the region, we did not anticipate sediment loads as great as observed at these sites. Further, ice lined the channel of Moose Creek until early June, which resulted in significant movement of the platform as the ice melted. A change in the deployment strategy would allow positioning of sensors at mid-depth in the water column to minimize the observed clogging of anti-fouling brushes with sediments from the streambed and would reduce changes in position of the sensors during deployment. Securing sensors to infrastructure would also ensure that sensors can be accessed for servicing during all flow conditions and minimize disruptions to power supplies.

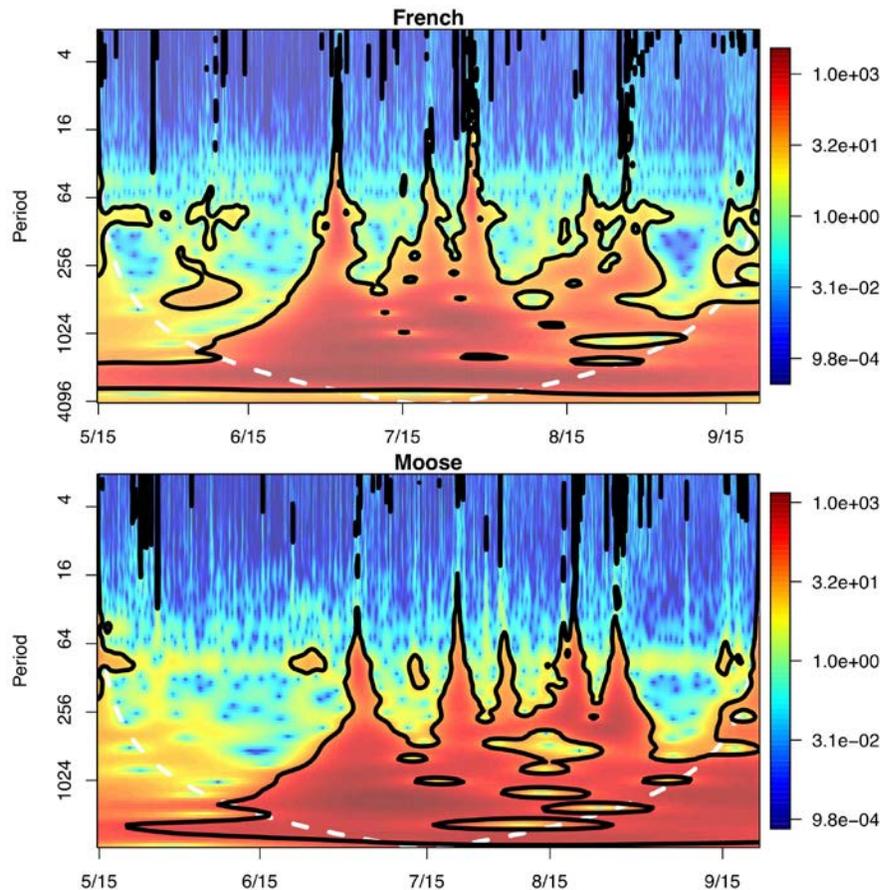


Fig. 8. Wavelet transform of fDOM concentration. Data were collected at 15-minute intervals; periods labeled on the y-axis correspond to 1 h, 4 h, 16 h, 64 h (~3 d), and 256 h (~11 d). Color depicts the wavelet power, or squared amplitude of oscillation, in quinine sulfate units², with warmer colors depicting wider temporal variation. Bold black lines outline variance that exceeds the value expected from an auto-regressive (red noise) spectrum. The white line indicates the cone of influence, outside of which edge effects introduce bias into the calculated power.

Temporal patterns. A central finding of this Limited Scope project is that collection of data at 15-minuted intervals revealed temporal patterns not reflected by grab samples in this, or comparable monitoring programs (Figs. 5 & 6). First, diurnal patterns were apparent in temperature, nitrate, fDOM, and conductivity, but variation at this time scale is not captured by conventional monitoring programs. Diurnal oscillations in nitrate and fDOM are summarized by the wavelet transform, which indicates moderate power (square of the amplitude of the oscillation) associated with a period of 24 h (yellow band at a period of ~100 apparent across many sampling dates in Figs. 7 & 8). These oscillations were strongest for nitrate in the early season, and appeared again in late August and September for Moose Creek (Fig. 7). Diurnal patterns in fDOM persisted throughout the measurement period at both sites, except when interrupted by storms (Fig. 8). Whereas diurnal oscillations of this magnitude might not contribute significantly to variation in carbon and nitrogen fluxes from the catchments, they could provide insight that contributes to disentangling the hydrologic and biological mechanisms underlying patterns of elemental cycling [Heffernan and Cohen, 2010]. For example, negative correlation of nitrate concentration with temperature at the diurnal scale (Fig. 9) suggests a biotic

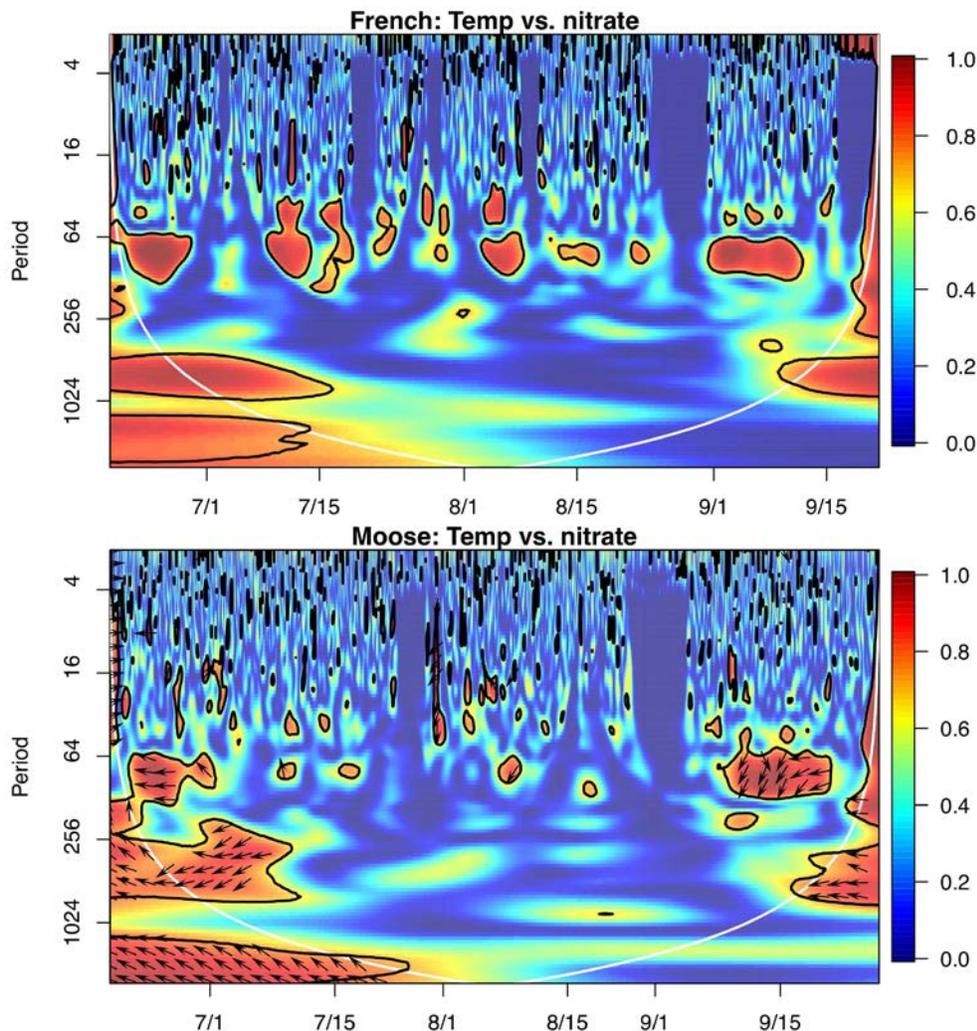


Fig. 9. Wavelet coherence plots depicting correlation of nitrate concentration and stream temperature for French (top) and Moose (bottom). The color ramp illustrates the correlation coefficient, with warm colors indicating a strong association between the two attributes. Left-pointing arrows indicate negative correlation and right-pointing arrows indicate positive correlation. Upward arrows indicate that temperature peaks lead nitrate peaks, whereas downward arrows indicate the opposite. Arrows are not rendered for French Creek due to missing data, but patterns in the direction of correlations were similar to Moose Creek.

role in the regulation of nitrate concentration at this time scale, as higher temperature would promote biological uptake of nitrate. Temperature was also correlated with fDOM concentration at the diurnal scale, but the correlation was negative during the thaw period of late May and early June, and positive during late summer (Fig. 10). A negative correlation of temperature and fDOM at the diurnal scale is likely driven by diurnal variations in streamflow, wherein peak runoff occurs when temperature is highest due to melting snow and ice, which dilutes the concentration of fDOM. A positive correlation of temperature and fDOM at the diurnal scale may arise because of release of organic matter from primary producers in the stream, which exhibit peak rates of production when light and temperature are at daily maxima.

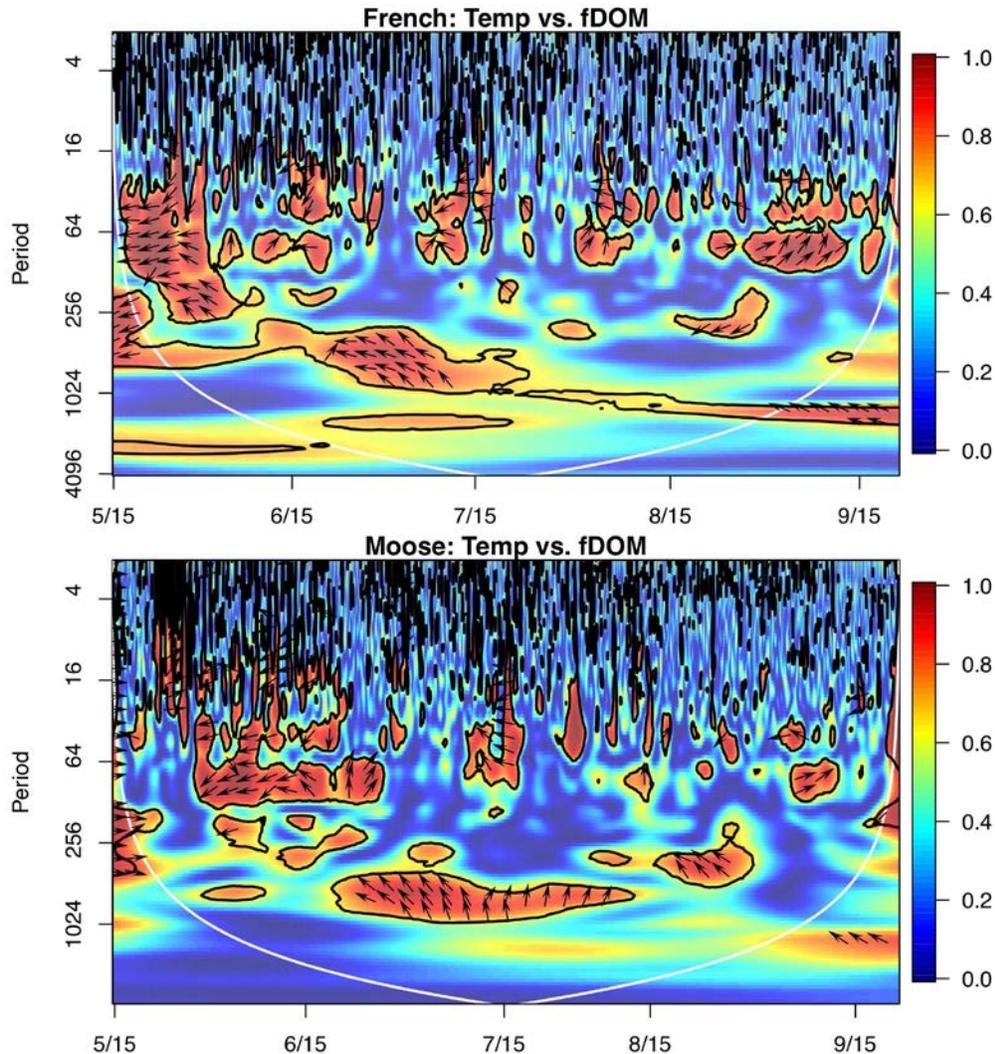


Fig. 10. Wavelet coherence plots depicting correlation of fDOM concentration and stream temperature for French (top) and Moose (bottom). The color ramp illustrates the correlation coefficient, with warm colors indicating a strong association between the two attributes. Left-pointing arrows indicate negative correlation and right-pointing arrows indicate positive correlation. Upward arrows indicate that temperature peaks lead fDOM peaks, whereas downward arrows indicate the opposite.

Storms interrupted the diurnal patterns in nitrate and fDOM concentration, and the strongest power (i.e., greatest variation in concentration) was associated with storms at both sites. The significant power at very low frequencies detected by the wavelet analysis is likely the result of transient sediment interference with the fDOM sensors and is not interpreted further here. Variation in fDOM concentration of high amplitude was associated with periods of days to weeks for both sites, and appears driven by large storm peaks that decline slowly to baseline concentrations of fDOM (Fig. 8). In contrast, storm-associated peaks in nitrate concentration were brief. These storm-generated peaks in concentration have significance for monitoring responses to disturbance. Brief peaks in nitrate concentration associated with storms were not captured by storm-triggered collections by autosamplers. Failure to capture these peaks would result in underestimates of nitrate fluxes.

Further, although pulses of fDOM triggered by storms were of longer duration than nitrate peaks and thus monitoring by grab samples would capture some part of the event, lower frequency sampling would fail to capture the maxima of such pulses, also leading to underestimates of fDOM concentration and flux in streams. In other catchments, peaks in nitrate concentration may also result from training activities associated with use of nitrate-based explosives such as occurs within the Yukon Training Area. Deployment of a nitrate sensor on Stuart Creek or similar sites in other regions would provide a means of monitoring the environmental effects of training missions.

Nitrate concentration increased over the seasonal period of observation in both streams (Figs. 5 & 6). Increased concentration of nitrate during the growing season in ecosystems characterized by nitrogen limitation, such as the boreal forest, is counter to nutrient retention theory, which suggests that forests should retain the limiting nutrient [Vitousek and Reiners, 1975]. Increasing availability of nitrate over summer supports the hypothesis that nitrogen escapes plant uptake as the depth of thawed soils increases and flowpaths bypass the shallow, biologically active soil horizons [Harms and Jones, 2012]. Nitrate in streams could also reflect increasing contribution of nitrogen-rich groundwater relative to surface runoff over the course of the summer, but this explanation seems less plausible because we did not observe a concomitant increase in conductivity of streamwater, which reflects the total solute load and is greater in groundwater than surface runoff. Finally, increased nitrate concentration in the streams could occur if uptake of nitrate within the stream channel declines as temperature decreased through the period of observation. We cannot further support or refute this mechanism with the data in-hand, but future measurement of dissolved oxygen would provide estimates of the demand for nitrogen by primary producers in the stream.

Inter-catchment comparisons. Mean concentrations of both fDOM and nitrate, and mean specific conductivity over the study period were greater in Moose than in French Creek. However, temporal patterns were remarkably similar, despite a 2-fold larger drainage area that was partially burned in Moose compared to the French site. Although others have observed increased nitrate concentration and decreased fDOM concentration in recently burned upland catchments of the region [Betts and Jones, 2009; Petrone et al., 2007], we observed no evidence of fire effects on the lowland Moose catchment. The stream was inaccessible at the burn perimeter, and monitoring below an unburned stand of forest may have buffered effects of the fire on stream chemistry, or biogeochemistry of lowland catchments responds differently to fire than uplands. Temporal patterns in specific conductivity and turbidity were conserved between the two sites, indicating similar hydrologic processes occurring in both catchments. Greater precipitation intensity during a late season storm at Moose compared to French might have produced the peak in nitrate that was observed in Moose but not in French, as the corresponding storm peak in turbidity and decline in conductivity due to dilution were greater in Moose than in French.

Table 1. Leading indicators of regime change calculated for the full period of observation.

	nitrate		fDOM		specific conductivity	
	<i>French</i>	<i>Moose</i>	<i>French</i>	<i>Moose</i>	<i>French</i>	<i>Moose</i>
standard deviation	7.7	8.5	30.0	33.7	17.7	20.6
skewness	2.1	0.0	0.8	0.3	-0.4	-0.2
kurtosis	20.7	8.1	0.1	-1.2	-1.0	-0.9
AR1	-0.4	-0.7	-0.5	-0.5	0.6	0.3

Several leading indicators of regime change were estimated to provide inter-catchment comparisons on the full season of observations (Table 1). Variance in concentrations of nitrate and fDOM as well as specific conductivity were similar at the seasonal scale between the two catchments, although wavelet analyses revealed differences between the catchments at shorter time scales. Skewness was greater for nitrate in French than in Moose Creek, due to the two large storm peaks that occurred in French Creek. Skew was also greater for fDOM in French, due to the larger peaks in concentration following storms. Kurtosis of nitrate observed across the seasonal time period was also much greater for French than Moose, again reflective of more extreme observations in the dataset. Kurtosis of fDOM concentration was negative in Moose, but low and positive in French, indicating fewer extreme values in Moose. Patterns in skew and kurtosis indicate that fDOM and nitrate in the French Creek catchment are more responsive to storms, which is likely due to smaller catchment area that does not buffer biogeochemical responses to storms. In contrast, specific conductivity showed similar values of skew and kurtosis between catchments, indicative of similar hydrologic functioning in the two catchments. The AR1 coefficient indicated negative autocorrelation between successive observations at 15-minute increments for fDOM and nitrate of similar magnitudes in both catchments, but positive autocorrelation for specific conductivity.

In sum, the leading indicators of regime change did not indicate that recent fire resulted in increased variance, observation of more extreme values, or “critical slowing down,” at least at the seasonal scale. Multiple years of record might provide a more appropriate time scale for evaluating dynamics following disturbance by fire. However, differences in the distributions of nitrate and fDOM concentrations that were apparent between the catchments at the seasonal scale potentially indicate the role of catchment size in contributing to stable output of carbon and nitrogen from catchments and buffering the magnitude of storm pulses. Similar behavior has been observed in other regions and is hypothesized to result from the effects of larger riparian areas in larger catchments, which can more strongly retain carbon and nutrients before they reach streams [Meixner and Fenn, 2004]. A more developed riparian zone is indicated by greater cover of woody wetlands in the Moose than French catchment (Fig. 1), particularly near the location of instream monitoring.

Conclusions and Implications for Future Research

This Limited Scope project indicates that instream sensors can be implemented for cost-effective monitoring of stream chemistry in high-latitude streams of the boreal forest. Collection of high-frequency data revealed patterns not captured by routine monitoring programs. These patterns included diurnal oscillations that are key for producing mechanistic understanding of elemental cycles in catchments. Sensors also captured peak concentrations of nitrate and fDOM

during storms that would be missed by conventional monitoring programs, but that may contribute significantly to the total seasonal or annual flux of nitrogen and carbon from the catchments [Reynolds *et al.*, 2016]. Sensors provide a cost-effective means for capturing temporal patterns because they require less personnel time for collection of samples and analysis in the laboratory. High-frequency monitoring of stream solutes would support the stewardship goals of managing military lands by indicating particular times during which solute loads are elevated and training activities are likely to generate further disturbance to catchments or cause significant impairment of water quality in receiving streams. Monitoring of nitrate downstream of sites used for training exercises with nitrate-based explosives in particular would provide insight into the seasonal and weather conditions that minimize transport of nitrate to streams, thereby buffering streams from elevated nitrate loads.

Recommendations for improvement in the accuracy of data collected by the sensors include use of permanent fixtures for deploying sensors and further refinement of relationships between DOM composition and fDOM concentration measured by the sensor. Additionally, collaboration with a statistician specializing in signal processing could generate technical advances in automated detection of outliers and cleaning of the time series collected by sensors. Finally, continuous monitoring of dissolved oxygen and stream discharge would enhance ability to separate hydrologic and biotic mechanisms contributing to observed patterns in solute dynamics.

I propose that the next step in developing understanding of resilience of high-latitude elemental cycles to disturbance is implementation of a network of sensors targeting sites in various stages of recovery from fire and with varying spatial extent of permafrost. A network of sites would provide the contrasts in catchment settings and disturbance history necessary to develop mechanistic understanding that is not possible from the two sites studied in this Limited Scope project. Further, multiple years of data collection would potentially capture the effects of disturbances occurring in real time, including both the “presses” of climate change and gradual degradation of permafrost and the “pulse” disturbances of fire and formation of thermokarst features. Such understanding is necessary to predict subsequent changes in the carbon cycle, by explicitly accounting for carbon exported by streams [Butman *et al.*, 2016] and estimating fluxes of nitrogen that may fuel productivity in downstream ecosystems [McClelland *et al.*, 2014]. This Limited Scope project has set the stage for such a network by demonstrating accuracy of data collected by sensors from boreal streams, and providing examples of the multi-scale temporal patterns revealed by high-frequency data.

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