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Atmospheric deposition as a source of carbon and nutrients to barren, alpine soils of the Colorado Rocky Mountains

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Abstract

Many alpine areas are experiencing intense deglaciation, biogeochemical changes driven by temperature rise, and changes in atmospheric deposition. There is mounting evidence that the water quality of alpine streams may be related to these changes, including rising atmospheric deposition of carbon (C) and nutrients. Given that barren alpine soils can be severely C limited, we evaluated the magnitude and chemical quality of atmospheric deposition of C and nutrients to an alpine site, the Green Lake 4 catchment in the Colorado Rocky Mountains. Using a long-term dataset (2002–2010) of weekly atmospheric wet deposition and snowpack chemistry, we found that volume-weighted mean dissolved organic carbon (DOC) concentrations were approximately 1.0 mg $L^{-1}$and weekly concentrations reached peaks as high at 6–10 mg L^{-1} every summer. Total dissolved nitrogen concentration also peaked in the summer, whereas total dissolved phosphorus and calcium concentrations were highest in the spring. Relationships among DOC concentration, dissolved organic matter (DOM) fluorescence properties, and nitrate and sulfate concentrations suggest that pollutants from nearby urban and agricultural sources and organic aerosols derived from subalpine vegetation may influence high summer DOC wet deposition concentrations. Interestingly, high DOC concentrations were also recorded during "dust-in-snow" events in the spring. Detailed chemical and spectroscopic analyses conducted for samples collected in 2010 revealed that the DOM in many late spring and summer samples was less aromatic and polydisperse and of lower molecular weight than that of winter and fall samples and, therefore, likely to be more bioavailable to microbes in barren alpine soils. Bioavailability experiments with different types of atmospheric C sources are needed to better evaluate the substrate quality of atmospheric C inputs. Our C budget estimates for the Green Lake 4 catchment suggest that atmospheric deposition represents an average input of approximately 13 kg C ha^{-1} yr^{-1} that could be as high as 24 kg C ha^{-1} yr^{-1} in high dust years and approaches that of autotrophic C fixation in barren soils.

1 Introduction

Mountain and tundra areas ~~are virtually certain to~~ experience ~~some of the most~~ severe ecological impacts as a result of changes in climate (IPCC, 2007). In comparison to low elevation ecosystems, alpine environments, often located in remote, high elevation areas, are also particularly sensitive to atmospheric deposition (Psenner, 1999; Ballantyne et al., 2010; Mladenov et al., 2011).There is thus urgency to improve our understanding of how biogeochemical cycling in high elevation catchments will respond to a combination of climatic changes and changes in atmospheric deposition. For example, atmospheric deposition of nitrogen (N) to mountain catchments has caused numerous changes in ecosystem functions (Williams and Tonnessen, 2000; Baron et al., 2009; Elser et al., 2009). Among these are a trend of increasing nitrate export in surface waters that has been observed in many alpine and high elevation catchments, such as those in the Colorado Rocky Mountains, USA (Williams et al., 2011; Baron et al., 2009), the Alps of northern Italy (Rogora, 2007), and southern Norway (de Wit et al., 2007), for which the process-level controls are just beginning to be explored. Baron et al. (2009) suggested that observed increases in nitrate export from the high-elevation Loch Vale catchment in the Colorado Front Range were the result of warmer temperatures that are melting ice in glaciers and rock glaciers. They propose that the phenomenon observed in Loch Vale may be indicative of N release from ice features worldwide as mountain glaciers retreat. Caine (2011) has recently shown that in the Green Lake 4 (GL4) catchment of the Colorado Front Range, increasing air temperatures are melting glacial and permafrost ice, increasing the concentrations of both base cations and nitrate in the outflow of GL4. In the Sierra Nevada Mountains, USA, Sickman et al. (2003), and earlier studies by Brooks et al. (1996, 1997) in the Colorado Front Range of the Rocky Mountains provide strong evidence that microbiological processes may also explain the observed increased N export from high elevation catchments. Surprisingly, Schmidt et al. (2009a) showed that significant nitrification occurs in recently deglaciated soils even on days when the soil temperature (at 5 cm depth) ranged from −10 °C at night to +30 °C during the day. High elevation areas with little or no developed soils have shown large amounts of microbial activity (King et al., 2008; Nemergut et al., 2007), within a few years of deglaciation in some cases (Schmidt et al., 2008). Moreover, overall net production (primary production minus respiration) from alpine soils (Blanken et al., 2009) is negative, which means the C loss from microbial respiration probably exceeds the autotrophic C production in these systems.

Despite the high microbial activity observed in barren alpine soils, these environments and the microbial communities in them are also severely carbon-limited (Williams et al., 1997; Brooks and Williams, 1999; Williams et al., 2007; King et al., 2008). It is currently unclear how microbial communities in oligotrophic soils obtain the C and energy necessary to sustain life. In many regions, these soils are snow covered for more than 9 months of the year, and the short snow-free period provides limited time for the acquisition of C and nutrients (Ley et al., 2004). The C budget for alpine catchments is not well constrained, and mounting evidence for active C cycling in alpine lakes and soils suggests that allochthonous C delivery may be extremely important.

Atmospheric aerosol transport is one vector for the delivery of C and other nutrients to alpine areas. Whereas the inorganic fraction of atmospheric deposition is relatively well measured in the US, mainly in precipitation chemistry by the National Atmospheric Deposition Program (NADP; http://nadp.sws.uiuc.edu/), there are few quantitative studies of organic C in atmospheric deposition and even fewer for atmospheric deposition in alpine environments. Precipitation has been shown to be an important C input for carbon-poor environments, such as coastal areas (Kieber et al., 2006, 2007) and the open ocean (Willey et al., 2000; Economu and Mihalopoulos, 2002; Jurado et al., 2008). For alpine environments, Ley et al. (2004) in the Colorado Rocky Mountains and more recently Mladenov et al. (2009, 2010) in the Sierra Nevada of Spain reported that aeolian deposition comprised about 10 % to 17 % organic C. Lawrence et al. (2010) also found surprisingly high organic C content in dust deposition. Mladenov et al. (2009) used spectroscopic techniques (UV-vis absorbance and fluorescence) in combination with air mass backward trajectories to demonstrate that water soluble organic carbon (WSOC) from dust emitted in Africa and deposited at an alpine site in Spain contained substantial amounts of humic-like fluorescent compounds. The humic-like fraction (HULIS) of atmospheric aerosols is becoming increasingly studied, yet the sources and chemical quality of this fraction are still a matter of debate (Graber and Rudich, 2006). In arid regions of the western US and southern Europe, dust emissions can result in substantial nutrient subsidies in the form of Fe, P, and N (Neff et al., 2008; Lawrence and Neff, 2009; Ballantyne et al., 2010; Reche et al., 2009). Given phosphorus (P) limitation or co-limitation in many alpine areas (Elser et al., 2009; King et al., 2008), dust-derived and other atmospheric P inputs may be especially important.

Here we compile data from long term monitoring (2002–2010) of water quality in atmospheric wet deposition and the snowpack to investigate the importance of atmospheric wet and dry inputs of water-soluble organic carbon and nutrients, such as nitrogen, phosphorus, and calcium, for a remote, high-elevation watershed in the Colorado Rocky Mountains, USA. We also address the question of the ecological importance of atmospheric C inputs to alpine ecosystems by examining the molecular weight and optical spectroscopic properties of DOM in 2010.

2 Site Description

The upper Green Lakes Valley is an east-facing glacial valley, located on the Continental Divide in the Colorado Front Range (40° 03′ N, 105° 35′ W; Fig. 1). Named for a series of shallow paternoster lakes, the Green Lakes Valley is the headwaters of North Boulder Creek and lies within the City of Boulder Watershed. Green Lakes Valley is part of the Niwot Ridge (NWT) Long-Term Ecological Research (LTER) network site and also the Boulder Creek Critical Zone Observatory. The upper valley is approximately 225 ha in area, and the elevation ranges from 4084 m at the Continental Divide to 3515 m at the outlet of GL4 (Fig. 1).

The continental, high-mountain climate of Green Lakes Valley has been recorded continuously at the D-1 meteorological station on Niwot Ridge (Fig. 1) for over 40 years (Greenland, 1989). Mean annual temperature at D-1 is −3.7 °C (Williams et al., 1996b). Almost 80 % of the approximately 1000 mm of recorded annual precipitation falls as snow (Caine, 1996). The bulk snow pack temperature remains below 0 °C until late spring, introducing a lag in the hydrological cycle by concentrating the release of melt water in a short, intense period of runoff (Caine, 1996).

Niwot Ridge forms the northern boundary of the Green Lakes Valley, and is the site of other experimental areas, including snow lysimeters, a subnivean laboratory and an Aerometrics wet-chemistry precipitation collector at the Saddle CO02 site (3500 m; Fig. 1), operated as part of the NADP. The NWT LTER program operates a second Aerometrics wet-chemistry precipitation collector following NADP protocols at the Soddie site (3300 m). However, this site is not part of the NADP network, which allows the NWT LTER program to analyze wet deposition samples for solutes not analyzed as part of NADP, including dissolved organic carbon (DOC), dissolved organic nitrogen (DON), total dissolved phosphorus (TDP) and dissolved organic phosphorus (DOP), and stable water isotopes.

3 Methods

3.1 Sample collection

3.1.1 Precipitation and snow

Physical and chemical properties of snow are routinely measured on a weekly basis at the Saddle (elevation 3528 m a.s.l.) and Soddie (elevation 3345 m a.s.l.) sites on Niwot Ridge; detailed sampling protocols have been presented in Williams et al. (1999, 2009). Precipitation quantity is measured as part of the NWT LTER program. Weekly wet deposition quality is measured in samples collected in precipitation collectors at the NADP Saddle CO02 site and the NWT LTER Soddie site (Fig. 1). However, the first 200–300 mL of the NADP CO02 collector sample were reserved for the NADP and frequently there was not enough volume to ~~perform~~ DOC and other organic species ~~analyses~~. Therefore, this study reports results from the more complete dataset of the Soddie collector, located at treeline.

Snow ~~sampling~~ was ~~conducted~~ weekly at the SSW site adjacent to the Soddie collector and annually at the time of maximum accumulation (mid-May) at multiple sites (ARK, NAV, 084, 085, 087, 088, and adjacent to GL4 and Green Lake 5 (GL5); Fig. 1). Snow depth measurements were made at >500 sites in the GL4 catchment and those data were used to calculate the snow water equivalent (SWE). Here we present both precipitation and snowpack values from 2002 to 2010. For 2010 we also evaluated the quality of organic matter using a variety of techniques, which are presented below.

3.1.2 Surface water

From 2002 to 2010 surface waters were collected as grab samples at the outlet of GL4 (Fig. 1). Polyethylene bottles were soaked with deionized (DI) water overnight and then rinsed with DI water five times; bottles were further rinsed three times with sample water at the time of collection. Water samples for dissolved organic matter analyses were collected in precombusted amber glass bottles with Teflon-lined caps and filtered through precombusted glass fiber filters with a nominal pore size of 0.7 µm. Samples for stable water isotopes were collected in 30 mL borosilicate vials with airtight caps. All water samples were transported the same day as collection to our wet chemistry laboratory and stored at 4 °C until analysis. Similar to wet deposition samples, the quality of organic matter from the outlet of GL4 was evaluated for 2010.

3.2 Water chemistry analyses

All wet deposition, surface water, and snow samples were analyzed for pH, specific conductance, NH_4, Ca^{2+}, NO_3^-, SO_4^{2-}, DOC, POC, TDN, ~~DON,~~ PN, TDP, PP, and $\delta^{18}O$

at the Institute for Arctic and Alpine Research (INSTAAR) in Boulder, CO. Chemical analyses followed this protocol for all water samples including snow samples. Snow samples were stored frozen (−20 °C) for 1 to 2 months until analysis. Blank samples of distilled DI water stored in sample bags for the same amount of time showed no significant contamination from the bags (Williams et al., 1992). Snow samples were placed in covered polyethylene buckets and melted overnight at room temperature. Samples for chemical and nutrient content were analyzed at the Kiowa wet chemistry laboratory run by the Niwot Ridge (NWT) LTER program, following the protocols presented in Williams et al. (2006). Dissolved species of interest (DOC, TDN, and TDP) are referred to as water soluble compounds and particulate measurements (POC, PN, and PP) are referred to as "water insoluble" compounds. Specific conductance and pH were measured immediately after melting for snow or after return to the laboratory for water samples using the Gran titration technique. Subsamples were immediately filtered through pre-rinsed (300 mL), 47 mm Gelman A/E glass fiber filters with an effective pore size of 0.7 µm. Filtered samples were stored in the dark at 4 °C for subsequent analyses within 1 to 4 weeks. Base cations, including Ca^{2+}, were analyzed using a Perkin Elmer Analyst 100 Atomic Absorption Spectrometer with a detection limit of 0.41 µeq L^{-1}. NH_4 was measured on an OI Analytical Spectrophotometric Flow System IV Analyzer with a detection limit of 0.47 µeq L^{-1} for ammonium and 0.12 µmoles L^{-1} for silica. Nitrate and SO_4^{2-} were measured on a Metrohm 761 Compact Ion Chromatograph with detection limits of 0.04 and 0.05 µeq L^{-1}, respectively. Samples for DOC and TDN were filtered through pre-combusted Whatman GF/F filters with a nominal pore size of 0.7 µm. DOC and TDN were determined by high temperature catalytic oxidation using a Shimadzu TOC-V CSN Organic Carbon Analyzer. DOC and TDN detection limits are 0.06 mg C L^{-1} and 1.47 µeq L^{-1}, respectively. DON was calculated by subtracting measured total inorganic N from TDN. Analytical bias was assessed through charge balance calculations using calibrated standards. An ecosystem proficiency blind survey was performed June and July 2004 through Environment Canada to assess the accuracy of the anion and cation methodologies. Analytical precision for all solutes was within ±2 % and assessed with spikes, blanks, and replicates.

Isotopic analyses of ^{18}O were conducted on unfiltered samples using the CO_2–H_2O equilibration technique at the Stable Isotope Laboratory at INSTAAR. The ^{18}O values are expressed in conventional delta (δ) notation in units of per mil (‰) relative to Vienna standard mean ocean water (V-SMOW) with a precision of ±0.05 %:

$$\delta^{18}O = [(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{VSMOW}]/(^{18}O/^{16}O)_{VSMOW} \times 1000. \qquad (1)$$

3.3 Size exclusion chromatography

Size exclusion chromatography (SEC) analysis was performed on a Thermo Scientific HPLC system equipped with a photodiode array (PDA Plus detector) at Florida International University in Miami, FL using a method similar to Maie et al. (2004). Briefly, 100 µL of filtered water was injected onto an YMC-Pack Diol-120 column. The mobile phase, flow rate 0.7 mL min.$^{-1}$, was comprised of 0.05 M tris(hydroxymethyl)aminomethane (THAM) buffer adjusted to a pH of 7 with concentrated phosphoric acid. The UV-Vis detector collected the absorbance at 280 nm. Molecular weight averages and polydispersity were calculated from the sample chromatograms between retention times of 14–25 min according to Maie et al. (2004) using standards of polystyrene (MW = 1400, 4300, 6800, 13000, 36000 Da), blue dextran, and glycine. Average molecular weight values presented here serve as a guide along the MW continuum and are not actual values (e.g. Scully et al., 2004).

3.4 UV-vis absorbance measurements

UV-vis absorbance was determined from 200 to 900 nm in a 1 cm path length quartz cuvette using an Agilent 8453 UV-vis spectrophotometer. UV-vis absorbance was measured in duplicate for each sample and for the wavelength range of interest (250 to 500 nm) the standard deviations always were <1 % of the measured absorbance. The mean absorbance from 790 to 800 nm was subtracted from all spectral absorbance values to remove scattering effects (Mitchell et al., 2003). Absorbance at 250 nm and

320 nm wavelengths were expressed as Naperian absorption coefficients (a_{250} and a_{320}) and are reported in the Supplement. Absorption at 250 nm reflects absorbance by aromatic moieties, and absorption at 320 nm is commonly used to refer to UV transparency in the water column (Morris et al., 1995). We also calculated the specific UV absorbance (SUVA), a DOC concentration-normalized absorbance value at 254 nm as specified in Weishaar et al. (2003). The spectral slopes from 275 to 295 nm and 350 to 400 nm were calculated as the slope value of the linear regression of the log-transformed absorption spectra (Helms et al., 2008). A dimensionless parameter, the slope ratio (S_R), was calculated as the ratio of the slope of the shorter wavelength region (275–295 nm), $S_{275-295}$, to that of the longer wavelength region (350–400 nm), $S_{350-400}$, (Helms et al., 2008).

3.5 Fluorescence spectral acquisition

A fraction of CDOM that emits fluorescence when excited with UV and visible light is known as fluorescent DOM (FDOM) (Coble, 2007). Fluorescence spectroscopy provides compositional and chemical information about this fluorescing DOM pool. Excitation emission matrices (EEMs) are a 3-dimensional representation of fluorescence intensities scanned over a range of excitation/emission (ex/em) wavelengths. Prominent humic peaks have been identified, such as in Region A (at ex/em 240-260/380-460 nm) and Region C (at ex/em 320-350/420-480 nm) (Coble, 1996). Other peaks have been attributed to tyrosine and tryptophan amino acid-like fluorescence at ex/em 275/310 nm and 275/340 nm (Coble, 1996), but other compounds may also fluoresce in these low excitation/emission regions (Mladenov et al., 2011). EEMs were collected with a JY-Horiba Spex Fluoromax-3 spectrophotometer at room temperature using 5 nm excitation and emission slit widths, an integration time of 0.25 s, an excitation range of 240–450 nm at 10 nm increments, and an emission range of 300–560 nm at 2 nm increments. To correct for lamp spectral properties and to compare results with those reported in other studies, spectra were collected in signal-to-reference (S:R) mode with instrument-specific excitation and emission corrections applied during post-processing.

EEMs were normalized to the Raman area to account for lamp decay over time and to compare with other studies. Raman-normalized Milli-Q blanks were subtracted to remove the Raman scattering signal. Instrument-specific corrections, raman area normalization, blank subtraction, and generation of EEMs were performed using MATLAB (version R2009b). We determined the two-dimensional fluorescence index (FI) to evaluate microbial and terrestrial contributions to the DOM pool (McKnight et al., 2001). The FI was calculated as the ratio of fluorescence intensities at 470 nm to 520 nm for an excitation at 370 nm. After all corrections, EEM spectra are highly reproducible with a standard error for FI of <0.02.

3.6 PARAFAC model

EEM spectral acquisition together with parallel factor analysis (PARAFAC) modeling was used to obtain quantitative information about the distribution of fluorescent components (Stedmon et al., 2003). The remote lake PARAFAC model, described in Mladenov et al. (2011), included 105 remote and high elevation alpine lakes samples and was validated using split-half validation and random initialization according to Stedmon and Bro (2008). PARAFAC distributions were obtained by fitting each EEM to the model, and fits were considered suitable if intensities in the residual EEMs, generated by subtracting the PARAFAC modeled EEM from the measured EEM, were <10 % of measured intensities. PARAFAC components and their excitation and emission maxima are plotted in Supplement Fig. S1. At low emission wavelengths (<350 nm), fluorescent signatures of the plastic NADP bucket blank were high when water was in contact with the bucket for up to one week (Supplement, Fig. S2). Therefore, we did not use spectral information acquired at wavelengths <350 nm. Here we report the total fluorescence (F_{total}) and the fluorescence loading of each relevant component with a peak >350 nm emission (LC1, LC2, LC3) in Raman units (RU). The standard error, calculated from the PARAFAC distributions of duplicate EEMs, associated with relative amounts of each component is <0.5 %.

3.7 Statistical analyses

To examine significant differences, categorized means with 95 % confidence intervals were calculated. One-way ANOVA analyses with site or season as the categorical predictor was used in combination with an unequal N HSD post-hoc test to evaluate significance of differences. Bivariate correlations, linear regressions and all other statistical analyses were performed with Statistica 9.

3.8 Backward trajectory analyses

We examined the source of air masses over Niwot Ridge in the Colorado Rocky Mountains (40.05° N, 105.57° W) by computing four consecutive backward trajectories (http://www.arl.noaa.gov/ready.html) on dates with precipitation. Trajectories were computed at 6 hour intervals using the HYSPLIT model (Draxler and Rolph 2003) and archived data from the Global Data Assimilation System (GDAS) meteorological dataset with 48 h run time. Exact dates of precipitation were identified from precipitation gage data at 10 min intervals measured at the Soddie site and made available through the NWT LTER.

3.9 Volume-weighted mean concentrations, loadings, and yields of soluble species

Annual volume-weighted mean concentrations of solutes in wet deposition were calculated as the sum of the product of weekly solute concentrations and weekly wet deposition volumes divided by the sum of weekly wet deposition volume values for each year. Annual volume-weighted mean concentrations of solutes in GL4 were calculated as the sum of the product of weekly solute concentrations and weekly discharge at the outlet of GL4 divided by the sum of weekly discharge from the lake for each year. Annual loadings of solutes in wet deposition to the GL4 catchment were calculated as the sum of weekly loadings. Weekly loadings of solutes were calculated by multiplying the precipitation-weighted mean solute concentration (mg L^{-1}) by the total gauge precipitation amount in centimeters for the summary period and dividing by 10, as per NADP protocols (http://nadp.sws.uiuc.edu/documentation/notes-depo.html). Solute yields from GL4 were calculated as the product of daily lake solute concentrations and daily discharge from the lake, summed for the entire snow-free period. ~~For total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP), molar concentrations were converted to~~ mass concentrations ~~by multiplying by the atomic weights, 14 g N mol^{-1} and 31 g P mol^{-1}, respectively. For total dissolved calcium (Ca), equivalent concentrations were converted to mass concentrations by multiplying by atomic weight, 40 g Ca mol^{-1}, and normalizing to the valence, 2.~~

3.10 Dry deposition loading

The dry deposition~~-derived mass loading~~ of water soluble compounds in the snowpack at maximum accumulation (between the end of October (approximate start of snow accumulation) and mid-May (approximate date of maximum accumulation of the snowpack)), $M_{\mathrm{max-dryWS}}$, was calculated as the difference between the total solute mass in the snow at maximum accumulation, $M_{\mathrm{max-snow}}$, and the cumulative solute mass in wet deposition (mainly snow) at maximum accumulation, $M_{\mathrm{max-wet}}$, as follows:

$$M_{\mathrm{max-dryWS}} = M_{\mathrm{max-snow}} - M_{\mathrm{max-wet}}. \tag{2}$$

The annual dry deposition mass loading of water soluble compounds, $M_{\mathrm{annual-dryWS}}$, was then calculated as follows:

$$M_{\mathrm{annual-dryWS}} = M_{\mathrm{max-dryWS}}(M_{\mathrm{annual-wet}} : M_{\mathrm{max-wet}}), \tag{3}$$

where $M_{\mathrm{annual-wet}} : M_{\mathrm{max-wet}}$ is the ratio of the mean annual wet deposition loading to the cumulative wet deposition loading at maximum accumulation.

The dry deposition-derived mass loading of water insoluble compounds in the snowpack at maximum accumulation (between the end of October (approximate start of

snow accumulation) and mid-May (approximate date of maximum accumulation of the snowpack)), $M_{\mathrm{max-dryWIN}}$, was taken as the particulate fraction of each solute. Particulate organic carbon (POC), particulate nitrogen (PN), and particulate phosphorus (PP) concentrations were measured in the snowpack at maximum accumulation from 2002–2004. The annual dry deposition mass loading of water insoluble compounds, $M_{\mathrm{annual-dryWIN}}$, was then calculated as follows:

$$M_{\mathrm{annual-dryWIN}} = M_{\mathrm{max-dryWIN}}(M_{\mathrm{annual-wet}} : M_{\mathrm{max-wet}}). \tag{4}$$

4 Results

4.1 DOM and nutrients in wet deposition and snowpack

Mean DOC, TDN, TDP, and Ca^{2+} concentrations measured at the Soddie collector were nearly identical to those measured at the NADP CO02 collector (Supplement Fig. S3) even though there is an elevational difference of almost 200 m between the two collectors. During the 2002 to 2010 period, the annual VWM DOC concentration in wet deposition at Soddie ranged from 0.77 to 1.41 mg C L^{-1} with a mean value of 1.12 mg C L^{-1} (Table 1). This value is substantially higher than mean DOC measured in coastal rain in New Zealand (0.7 mg C L^{-1}; Kieber et al., 2002) or the USA (∼0.6 mg C L^{-1}; Willey et al., 2000) and approaches the range of DOC in continental rain (∼2 mg C L^{-1}; Willey et al., 2000). Weekly DOC reached concentrations as high as ~~6–~~10 mg C L^{-1} (Fig. 2).

The DOC loading in wet deposition from 2002–2010 ranged from 5.7 to 19 kg C ha^{-1} yr^{-1} with a mean value of 9.9 kg C ha^{-1} yr^{-1} (Table 1) and represented the greatest loading of all solutes in wet deposition (Supplement Table S1). The highest annual DOC loading in wet deposition was measured in 2006, a year with high dust activity (Rhoades et al., 2010). Mean TDN and Ca^{2+} loadings were 3.8 kg N ha^{-1} yr^{-1} and 2.7 kg Ca^{2+} ha^{-1} yr^{-1}, respectively (Table 1), whereas DON, TDP, DOP loadings were orders of magnitude lower (Supplement Table S1).

Wet deposition ~~represents an~~ input ~~of~~ 2224 kg C yr^{-1}, 850 kg N yr^{-1} , 7 kg P yr^{-1} and 599 kg Ca^{2+} yr^{-1} to the 225 ha GL4 catchment (Table 1). Annual yields of DOC, TDN, TDP, and Ca^{2+} in GL4 were 2007 kg C, 693 kg N, 5.78 kg P, and 4604 kg Ca^{2+} (Table 2). A comparison of wet deposition and lake yield showed that atmospheric ~~loadings~~ of DOC, TDN, and TDP ~~were~~ on the same order of magnitude as yields from the lake (Table 2). Ca^{2+} in wet deposition was nearly an order of magnitude lower than yield of Ca^{2+} from the lake (Table 2).

The cumulative DOC ~~loading~~ in snow at maximum accumulation, calculated from DOC concentrations measured just prior to the ionic pulse (Williams et al., 2009) (Table 3) ranged from 2.0 to 6.1 kg C ha^{-1} yr^{-1} during the 2002–2010 period, with a mean value of 3.5 kg C ha^{-1} yr^{-1} (Table 4). For TDN and TDP, ~~the loadings~~ ranged from 1.0 to 2.3 kg N ha^{-1} yr^{-1} and 0.02 to 0.05 kg P ha^{-1} yr^{-1} (Table 4). Ca^{2+} ~~loadings~~ in snow at maximum accumulation ranged from 0.8 to 3.7 kg Ca^{2+} ha^{-1} yr^{-1} and were highest in 2006 and 2010 (Table 4). Applying the average rates equally over the entire GL4 catchment, ~~these loadings corresponds to~~ 788 kg C yr^{-1}, 351 kg N yr^{-1}, 8 kg P yr^{-1} and 438 kg Ca yr^{-1}, in the snowpack of the catchment at maximum accumulation (Table 4).

4.2 Seasonal dynamics in wet deposition

DOC concentrations in wet deposition showed a seasonal cycle of minima in the winter and maxima in the summer (Fig. 2). Wet deposition DOC ~~loadings were~~ significantly higher in the summer, particularly in July, than in other seasons (Fig. 3). Peaks in TDN concentrations were observed in the summer and Ca^{2+} concentration peaks were observed in the spring (Fig. 2). TDP concentrations did not have a seasonal cycle, but most peaks occurred during the spring (Fig. 2). TDN and DON loadings were significantly higher in the summer than in the winter (Fig. 3). In contrast, Ca^{2+} loadings were significantly higher in the spring than in all other seasons (Fig. 3). The highest DOP ~~loadings were~~ also in the spring and these were significantly higher than in the fall or winter (Fig. 3). Whereas DOC:TDN ratios were low, around 2 to 4, DOC:DON ratios were extremely high, often greater than 100 in the spring and summer (Fig. 4). Summer

months also had significantly higher DOC:TDN, DOC:TDP, TDN:TDP, DOC:DOP, and DON:DOP ratios than other seasons (Fig. 4).

DOC plotted against wet deposition volume and $\delta^{18}O$ show that the highest DOC loadings (Fig. 5) were observed in the summer when $\delta^{18}O$ values were most enriched (from 0 ‰ to −15 ‰). A contrasting effect was observed in the case of Ca^{2+} concentrations, which were highest in the spring and corresponded to lighter $\delta^{18}O$ values of −10 ‰ to −20 ‰ (Fig. 5). On 25 June 2002 and on 21 February 2006, two of the highest Ca^{2+} concentrations (202 ueq L^{-1} and 534 ueq L^{-1}) corresponded to two of the highest DOC concentrations (10.9 mg C L^{-1} and 7.1 mg C L^{-1}, respectively). The 2006 peak occurred during a “dust-in-snow” deposition event (Rhoades et al., 2010), ~~which we define as~~ an event during which dust particles were deposited with precipitation, as opposed to ~~falling~~ on the surface of the snow (dust-on-snow).

Linear regressions between DOC concentrations and concentrations of inorganic N (as NO_3^-), SO_4^{2-}, Ca^{2+}, and Si^+ were significantly and positively correlated in the summer (Fig. 6). During spring and winter seasons, these relationships were insignificant, and in the fall relationships were much less significant ($r^2 \leq 0.35$ for all).

4.3 Dissolved organic matter quality in wet deposition and the lake

DOC concentrations in wet deposition in 2010 peaked in the spring and summer (25 May, 20 July, and 27 July), similar to other years. SUVA values~~, indicative of the degree of aromaticity (Weishaar et al., 2003),~~ ranged from 0.1 to 2.6 L mg^{-1} m^{-1} and, in general, summer samples had the lowest SUVA values (Fig. 7). S_R values~~, which increase with greater photobleaching and lower molecular weight (Helms et al., 2008),~~ ranged from 0.8 to 2.9 with a mean value of 1.6 (Supplement Table S3). Mean $S_{275-295}$ and $S_{350-400}$ values were 0.018 nm^{-1} and 0.012 nm^{-1}, respectively (Supplement Table S3). FI values ranged from 1.20 to 1.55 and showed great variability from week to week but no seasonal pattern (Fig. 7). In contrast to the fairly low SUVA values and highly variable FI in wet deposition, DOM in GL4 had fairly stable SUVA and FI values prior to snowmelt, (means of 1.4 L mg C^{-1} m^{-1} and 1.48, respectively), which shifted to higher

SUVA values (mean of 3.6 L mg C^{-1} m^{-1}) and lower, but still stable, FI values (mean of 1.37) after snowmelt (Fig. 7).

SEC analyses showed that during the late spring and summer of 2010, the DOM in wet deposition was of fairly moderate molecular weight (800–1200 Da; Fig. 7) and polydispersity (Supplement Table S3). Samples collected during the fall and winter of 2010 were of much higher molecular weight (>1200 Da; Supplement Table S3). Average molecular weight and polydispersity were well correlated ($p < 0.01$, $r = 0.938$) indicating that samples with higher average molecular weights, i.e. samples collected in the fall/winter, contained a more heterogeneous mixture of DOM.

EEMs from different dates of wet deposition also showed fairly diverse spectra (Fig. 8). Fitting to a PARAFAC model developed specifically for alpine watersheds identified C2, a fulvic-like component with an ex/em peak at <240(290)/406 nm that appears to be derived from both microbial and terrestrial sources (Mladenov et al., 2011; similar to C3 in Yamashita and Jaffe, 2008), as the most dominant component, representing 55 ± 9 % of the total fluorescence (Supplement Table S3). The concentration of C2 was significantly and positively related to DOC concentration (Fig. 10). C1, a component with an ex/em peak at <240(340)/492 nm that is related to terrestrial humic-like fluorescence in Yamashita and Jaffe (2008) and to the aerosol index in Mladenov et al. (2011), represented 28 ± 9 % of the total fluorescence and its concentration was significantly and positively related to sulfate (Fig. 10). C1 was also negatively related to polydispersity (Fig. 9) and molecular weight. C3 (see C5 in Mladenov et al., 2011), a component with an ex/em peak at 340/414 nm that was found to be highly correlated to aromatic and phenolic C content (see C5 in Fellman et al. (2010)), represented 18 ±4 % and its concentration was significantly and positively related to nitrate (Fig. 9). C3 is also in the range of the HULIS component identified in Muller et al. (2008), which was found to increase under conditions of stagnant air and build up of pollutants in the atmosphere. Microbial, tyrosine-like and tryptophan-like components from the PARAFAC model (Mladenov et al., 2011) had maxima <350 nm emission and were excluded from this analysis.

4.4 Dry deposition estimates

The amount of DOC in wet deposition between the end of October (approximate start of snow accumulation) and end of May (approximate date of maximum accumulation of the snowpack) or $M_{\text{max-wet}}$ was 3.6 kg C ha^{-1} (Table 5). We assumed that the difference between total DOC in the snow at maximum accumulation, $M_{\text{max-snow}}$, and $M_{\text{max-wet}}$ was due to dry deposition inputs to the snowpack, $M_{\text{max-dryWSOC}}$. Using the mean values for 2002–2010, $M_{\text{max-dryWSOC}}$ was zero. However, for 2006, the year with the highest DOC loading in wet deposition and fairly high dust activity, $M_{\text{max-dryWSOC}}$ was 1.3 kg C ha^{-1}. ~~Using the ratio, $M_{\text{annual-wet}}$:$M_{\text{max-wet}}$,~~ the 2006 dry deposition WSOC loading, $M_{\text{annual-dryWSOC}}$, was estimated at 5.2 kg C ha^{-1}. Using the same extrapolation, the mean particulate organic carbon (POC) loading, which represents the WINSOC input from dry deposition to the snowpack, was almost 3.0 kg WINSOC ha^{-1}. For the GL4 watershed, the annual WSOC and WINSOC loading from dry deposition represents an input of approximately 600 kg DOC to the watershed (Table 5).

We applied the above approach to also estimate TDN, TDP and total dissolved Ca^{2+} dry deposition-derived inputs. First, the wet deposition inputs of TDN, TDP and Ca were calculated through mid-May (time of maximum accumulation) and represented on average 1.9 kg TDN ha^{-1}, 0.01 kg TDP ha^{-1}, and 2.0 kg Ca^{2+} ha^{-1}. For TDN and Ca^{2+}, $M_{\text{max-wet}}$ values were greater than or equal to $M_{\text{max-snow}}$ and $M_{\text{max-dryWS}}$ was essentially zero (Table 5). However, for TDP, the water soluble fraction of dry deposition (0.07 kg TDP ha^{-1}) was estimated to be more than twice that of wet deposition (0.03 kg TDP ha^{-1}; Table 5). From the particulate (water insoluble) fractions of TDN and TDP, we calculated that 0.5 kg TDN ha^{-1} and 0.05 kg TDP ha^{-1} may be delivered to the GL4 catchment from dry deposition.

5 Discussion

Here we show new evidence that atmospheric wet and dry deposition of C but also N, P, and Ca^{2+} are important inputs of these elements to the carbon-poor and barren alpine soils at Niwot Ridge. In terms of DOC concentrations, the summer wet deposition values we measured, ranging from 4–10 mg C L^{-1}, were higher than DOC concentrations in GL4 and the snowpack and are high enough to be comparable to DOC concentrations found in temperate lakes (Sobek et al., 2007). Seasonal patterns were also present for other solutes in wet deposition, with loadings of TDN and DON also consistently highest in the summer.

Summertime evapoconcentration of inorganic and organic particles in the atmosphere may have some bearing on the high summer DOC concentrations. In the summer, precipitation is most enriched in $\delta^{18}O$ (Fig. 5), and such enrichment may reflect higher atmospheric aerosol concentrations resulting from evapoconcentration. Levin et al. (2009) also reported higher aerosol concentrations in Rocky Mountain National Park in the summer than in the spring, composed mainly of organic species. However, not all solutes in our study peak in the summer or when $\delta^{18}O$ values are enriched (e.g. TDP, DOP, and Ca^{2+}), and, consequently, varying aerosol sources must be considered in addition to evapoconcentration effects.

5.1 Air pollution, dust-in-snow, and other sources of atmospheric deposition

The seasonal variability in DOM quality (FI, SUVA, MW) suggests that the C sources for atmospheric deposition are ~~probably~~ highly variable. High summer DOC concentrations may be related in part to the higher summer biological emissions and concentrations of biological particles in the atmosphere. Peak pollen shedding at treeline in Colorado occurs in June and July and the leachable carbon from pollen may contribute to DOC in deposition during these months. There is certainly anecdotal evidence of pollen in June and July wet deposition from observations of "yellow particles" in the collectors and retained on filters during this time (K. Chowanski and C. Seibold, personal communication, 2010). Kieber et al. (2002) and Willey et al. (2000) also observed higher DOC concentrations in summer rainfall that were attributed to terrestrially-derived continental sources.

One pathway for organic aerosol formation that has been observed at Niwot Ridge (Boy et al., 2008) and may be especially important during summer months is via reactions between atmospheric sulfuric acid and sesquiterpenes from sub-alpine vegetation. High summer concentrations of nitrogen and sulfur species in the atmosphere and in wet deposition attributed to urban and agricultural pollution have been measured at high elevation sites in the Colorado Rocky Mountains (Malm et al., 2010; Beem et al., 2010). The prevailing winds at Niwot Ridge are almost exclusively westerlies during winter months, but there is a switch to occasional upslope (easterly) winds in the daytime during summer months (Blanken et al., 2009), which may transport urban and agricultural pollutants (NO_x and SO_x) to higher elevations. Photochemistry is needed to further oxidize the sulfur species required for new particle growth, and, indeed, we found a strong UV radiation influence on DOM in wet deposition, especially during the summer (see next section). Another source of organic matter in atmospheric deposition may be the organic pollutants themselves, which may be transported to higher elevations under upslope conditions. From our observations it is ~~difficult~~ to tell whether we are measuring urban carbonaceous pollutants or organic aerosols formed from reactions between vegetation-derived emissions and NO_x and SO_x. Willey et al. (2000) showed significant correlations between DOC concentrations and pollutant components, such as hydrogen ion, nitrate, and non-sea salt sulfate in summer non-tropical rain. Likewise, our correlations between DOC, in terms of both its concentration and quality (terrestrial humic-like C1 and phenolic and aromatic C3 fluorescent components), and SO_4^{2-} and NO_3^- in the summer (Fig. 6) support both interpretations. ~~Future radiocarbon analyses will provide an additional line of evidence to help distinguish organic aerosol sources and resolve whether HULIS is uniquely derived from terrestrial humics in vegetation or if urban and agricultural pollution may have some influence on HULIS in the atmosphere.~~

In the spring, both inorganic and organic compounds are delivered in wet and dry deposition associated with dust. High Ca^{2+} and DOP content is characteristic of dust deposition to the Colorado Rocky Mountains from the Colorado Plateau and Mojave Desert (Lawrence et al., 2010), which is most pronounced during the spring. Three high Ca^{2+} precipitation events measured in 2010 (4, 11, and 18 May) had backward trajectories showing a Colorado Plateau air mass source (Supplement Fig. S4). Dust and biological particles are known ice nuclei (Prenni et al., 2009) with a direct influence on regional precipitation. Therefore it is not surprising that there are recurring springtime wet deposition peaks in Ca^{2+} and DOP (Fig. 3) that reflect springtime "dust-in-snow" events. Without question, the Ca^{2+}, DOP, and other aeolian rock- or soil-derived inputs associated with dust, are constituents in wet and dry deposition whose influence on remote alpine sites should be further evaluated in light of their importance for ecosystem functioning (Morales-Baquero et al., 2006; Pulido-Villena et al., 2006).

In the spring, organic aerosols associated with dust may also be important sources of organic carbon in both wet and dry deposition. The three "dust-in-snow" events of ~~0~~4, 11 and 18 May 2010 had relatively high DOC loadings at 272, 137 and 415 g C ha^{-1} wk^{-1}, respectively. The EEMs for these dates resembled those from Saharan wet deposition (Mladenov et al., 2009) with a shoulder at ex/em 305/425 nm and a broad peak centered at approximately ex/em <240/445 nm (see Fig. 8 for 11 May 2010 example). Another known dust-in-snow event, the storm of 21 Feb 2006 (Rhoades et al., 2010), was also associated with very high DOC concentrations and loadings (>7 mg C L^{-1} and 410 g ha^{-1} wk^{-1}). Dry deposition measured in dust collectors at Niwot Ridge contained roughly 10 % to 17 % organic material (Litaor et al., 1987; Ley et al., 2004). Estimates of 0.42 g OC m^{-2} yr^{-1} in dust reported by Ley et al. (2004) for Niwot Ridge are higher but comparable to the WINSOC loading in the snowpack at maximum accumulation measured in our study (0.28 g WINSOC m^{-2} yr^{-1}). Our results, however, are more spatially representative (from >6 sampling locations measured during three years). For the high dust year of 2006, the estimate of WSOC loading at maximum accumulation (0.52 g WSOC m^{-2} yr^{-1}) is much higher than average (Table 5)

and further demonstrates that there may also be a substantial pool of water soluble organic carbon released from dust-in-snow. These examples are consistent with recent hypotheses that dust transport is a vector for organic matter deposition globally (Mladenov et al., 2011).

5.2 Bioavailability of OC in atmospheric deposition

Given that there is a substantial amount of organic carbon in atmospheric deposition at ~~our alpine site~~, especially in the summer, what then is its bioavailability? Recent work (Willey et al., 2000), using low temperature dark incubations of rainfall samples, determined that 60 % of the DOC in coastal rainwater at Wilmington, North Carolina, USA was labile to microbial or chemical degradation. Our results from UV-vis absorbance spectroscopy indicate that the DOM in wet deposition is generally of low aromaticity (low SUVA values), which also supports this as a more labile C source. Such low SUVA values further suggest that wet deposition DOM has been photobleached by intense UV radiation, and the high S_R and $S_{275-295}$ values we observed are also consistent with DOM photobleaching (Helms et al., 2008). The greater blue-shifting (to shorter emission wavelengths) of dominant A and C peaks in the wet deposition EEMs is yet another indication of photo-oxidation processes that act to decrease aromaticity. The decrease in aromatic rings and other structural changes that reduce the extent of the π-electron system will increase the energy difference between ground state and the first excited state, which leads to blue-shifted fluorescence emission (Coble, 1996). In addition to potentially improving the substrate quality of organic aerosols via destruction of aromatic rings, photobleaching of organic compounds in the atmosphere may further influence the high summer DOC:DON ratios (mean >100) we observed, by removing N. This situation has been observed in lakes with extensive solar exposure (Waiser and Robarts, 2000). Organic compounds derived from industrial pollution tend to have high carbon content with low reactive organic N content (Aiken et al., 2008; Beem et al., 2010) and this may also explain the high Redfield ratios we observed.

Molecular weight provides another indication of DOM bioavailability, as lower MW compounds are typically more labile to microbial degradation (Amon and Benner, 1996). It has also been suggested that biologically labile and less polydisperse DOM will result from photolysis reactions (Chin et al., 1998). Recent studies have found that the MW of water-soluble atmospheric macromolecular compounds is typically not higher than 500–700 Da (Kiss et al., 2003; Zamburova et al., 2005). MW measurements are highly method-dependent and the higher overall MW values we observed may be influenced by our use of high MW standards (Zamburova et al., 2005). Despite the fact that our MW values are high relative to those of other studies (Kiss et al., 2003; Zamburova et al., 2005), our measurements of lower MW and polydispersity in the summer and late spring (than in fall and winter) argue for greater bioavailability of wet deposition DOM during those seasons. In contrast, compounds from the fall and winter generally had higher MW and polydispersity, suggesting larger and more heterogeneous structures, which may be more recalcitrant to microbial degradation. Despite the high summer Redfield ratios, the lower MW DOM deposited to barren soils in the summer may be labile to certain microbial communities. In C-limited soils, the addition of C alone (without N) has been shown stimulate bacteria and fungi, with bacteria responding to a more easily available C source (glucose) and fungi favoring a more complex C source (cellulose) (Meidute et al., 2008). At our site, fungi may have an important role. Chytrids have been found to dominate the fungal biodiversity at Niwot Ridge (Freeman et al., 2009a) and are known to be partially supported by aeolian inputs, such as pollen. Also, alpine heterotrophic bacteria such as *Polaromonas*, found at Niwot Ridge and other barren alpine environments, can oxidize even recalcitrant carbon sources (Darcy et al., 2011 and references therein). ~~Upcoming bioavailability experiments with different types of atmospheric C sources will help us shed light on the substrate quality of atmospheric C inputs.~~

5.3 Relevance of atmospheric wet and dry deposition inputs for the catchment

To assess the relevance of atmospheric inputs of C compared to other inputs and losses of C in the alpine, we estimated the total C budget for the GL4 catchment. For atmospheric deposition inputs to the GL4 catchment, we used values from the Soddie collector, which were nearly identical to those measured at the NADP CO02 collector. Together, the wet and dry deposition inputs were 2800 kg C (13 kg C ha^{-1} yr^{-1}) on average and ranged from 1500 kg C (7 kg C ha^{-1} yr^{-1}) to >5400 kg C (24 kg C ha^{-1} yr^{-1}) (Table 5; Fig. 10). Whereas atmospheric deposition occurs throughout the year and across the entire landscape, primary production in barren soils is more patchy, occurring mainly during the summer snow-free period (approximately 90 d) (Freeman et al., 2009b) and over an area~~l extent~~ that is about half the talus area or roughly 20 % of the watershed area (Erickson et al., 2005). Our calculations show that soil primary production inputs of approximately 10 800 kg C (calculated using the production rate of 240 kg C ha^{-1} yr^{-1} from Freeman et al. (2009b) over 20 % of the watershed) are indeed the highest inputs, as suggested by Freeman et al. (2009b). For barren soils, respiration C losses were calculated at approximately 12 600 kg C, using an average 2002 summer season respiration rate of 0.013 g C m^{-2} hr^{-1} (Freeman et al., 2009a), estimated to also occur for 90 d and over 20 % of the watershed area. According to Caine (1995, and references therein), roughly 20 % of the catchment also comprises low-lying vegetation. As data were not available for primary production or respiration from aboveground vegetation, for the purposes of this C budget estimate, we assumed that this aboveground C input and loss were approximately equal. Data for lake primary production and respiration were also not available. However, Ask et al. (2009) reported that the flux of C (production minus respiration) from clear, oligotrophic lakes in the arctic was net negative. Using their estimates of 60 g OC m^{-2} lake area yr^{-1}, we calculated that lake respiration exceeded lake production by approximately 700 kg C each year (Fig. 10). Finally, we used the value of DOC export from GL4 to represent the annual export of DOC from the watershed or approximately 2000 kg C yr^{-1} (Fig. 10).

Taking ~~together~~ all inputs and losses of C and noting that there is also a pool of soil organic C that may not be at steady state, we concluded that our C budget is roughly balanced and probably underestimates watershed C inputs. In particular, we expect that dry deposition C inputs, especially those from pollen transported to higher elevations during the summer, may be underestimated because they would not be captured in our calculations of WINSOC from POC in the snowpack at maximum accumulation. Using a conservative pollen deposition loading rate for a remote site in Wisconsin (0.35 $\mathrm{g\,C\,m^{-2}\,yr^{-1}}$; Doskey and Ugoagwu, 1989), the additional input to the GL4 watershed from pollen may be ~800 $\mathrm{kg\,C\,yr^{-1}}$. There are gaps in our understanding of aboveground C production and respiration in the more vegetated areas of the GL4 watershed and uncertainties in the alpine lake C flux that need also to be filled. Nevertheless, for the most barren and C-limited parts of the watershed, our C budget suggests that atmospheric C inputs are roughly 25 % of the C inputs from soil primary production, but that figure can be as high as 60 % (Fig. 5). Given their potential bioavailability, these inputs may be important for heterotrophs in this C-limited but dynamic alpine environment.

Atmospheric N deposition has been ~~extensively~~ studied in the GL4 watershed (e.g. Williams et al., 1996;, 2001; Darrouzet-Nardi et al., 2011). The combined wet and dry deposition N loading we measured (4.3 $\mathrm{kg\,N\,a^{-1}}$) is ~~exactly~~ in the range reported by Williams et al. (2001). Our results further suggest that although there is net retention of N in the catchment, as proposed by Williams et al. (2001), there is still substantial N export (at 690 $\mathrm{kg\,N\,yr^{-1}}$) from the catchment. In contrast, the retention of P in the GL4 catchment is much greater. Compared to the combined atmospheric inputs (34 $\mathrm{kg\,P\,yr^{-1}}$), the much lower export of P from GL4 (at 6 $\mathrm{kg\,P\,yr^{-1}}$) suggests that P is taken up in catchment soils and lakes. This high uptake of P (~80 % of the P input) suggests that atmospheric P inputs are important for meeting the P demand of heterotrophic microbial populations in the barren talus soils of Niwot Ridge, which have been shown to be limited mainly by C, but also by P (King et al., 2008). We hypothesize that, as a result of heterotrophic C processing, fueled by both atmospheric

C and P and autochthonous C sources, the heterotrophic waste products (ammonium compounds) become available to autotrophs, such as nitrifying Archaea and Bacteria. There is mounting evidence that nitrate export from Rocky Mountain catchments has been decoupled from atmospheric N deposition and is due in part to increased nitrification in these catchments (Baron et al., 2009; Williams et al., 2001). Indeed, we observed substantial N export from the GL4 catchment, as described earlier. This linkage between a cascade of processes – atmospheric delivery of C and nutrients, heterotrophic and autotrophic microbial dynamics in barren soils, N export from alpine catchments, and changing headwater quality~~ – is an important focus of our ongoing research~~.

6 Conclusions

Our results suggest that atmospheric deposition may represent a substantial input of C and nutrients to carbon-limited alpine environments. The strong seasonality in wet deposition DOC concentrations and loadings further suggests that DOC is a solute that should be routinely measured in monitoring programs. Our results also indicate that dry deposition, particularly dust deposition, may be important for delivering C and P to alpine environments. Although our research provides an initial estimate of dry deposition loadings, more efforts to quantify and constrain this input are needed. In terms of its bioavailability for alpine microorganisms, our results suggest that DOM in summer wet (and some spring) deposition events, which are potentially derived from air pollution, bioaerosol, and dust sources, are of lower MW and aromaticity and may be particularly labile to microbial degradation. The implications of microbial processing of allochthonous atmospheric inputs of C and other nutrients in alpine environments are extremely important for biogeochemical cycles and water quality in headwater catchments~~, and this topic is central to our ongoing research~~.

Supplementary material related to this article is available online at: http://www.biogeosciences-discuss.net/9/2375/2012/ bgd-9-2375-2012-supplement.pdf.

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References

Aiken, A. C., DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, Environ. Sci. Technol., 42, 4478–4485, 2008.

Amon, R. M. W. and Benner, R.: Bacterial Utilization of Different Size Classes of Dissolved Organic Matter, Limnol. Oceanogr., 41, 41–51, 1996.

Ask, J., Karlsson, J., Persson, L. Ask, P., Bystro, P., and Jansson, M.: Whole-lake estimates of carbon flux through algae and bacteria in benthic and pelagic habitats of clear-water lakes, Ecology, 90, 1923–1932, 2009.

Ballantyne, A. P., Brahney, J., Fernandez, D., Lawrence, C. L., Saros, J., and Neff, J. C.: Biogeochemical response of alpine lakes to a recent increase in dust deposition in the Southwestern, US, Biogeosciences, 8, 2689–2706, doi:10.5194/bg-8-2689-2011, 2011.

Baron, J. S., Schmidt, T. M., and Hartman, M. D.: Climate-induced changes in high elevation stream nitrate dynamics, Glob. Change Biol., 15, 1777–1789, doi:10.1111/j.1365-2486.2009.01847.x, 2009.

Beem, K. B., Raja, S., Schwandner, F. M., Taylor, C., Lee, T., Sullivan, A. P., Carrico, C. M., McMeeking, G. R., Day, D., Levin, E., Hand, J., Kreidenweis, S. M., Schichtel, B., Malm, W. C., and Collett Jr., J. L.: Deposition of reactive nitrogen during the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study, Environ. Pollut., 158, 862–872, 2010.

Blanken, P., Williams, M. W., Burns, S. P., Monson, R. K., Knowles, J., Chowanski, K., and Ackerman, T.: A comparison of water and carbon dioxide exchange at a windy alpine tundra and subalpine forest site near Niwot Ridge, Colorado, Biogeochemistry, 95, 61–76, doi:10.1007/s10533-009-9325-9, 2009.

Boy, M., Karl, T., Turnipseed, A., Mauldin, R. L., Kosciuch, E., Greenberg, J., Rathbone, J., Smith, J., Held, A., Barsanti, K., Wehner, B., Bauer, S., Wiedensohler, A., Bonn, B., Kulmala, M., and Guenther, A.: New particle formation in the Front Range of the Colorado Rocky Mountains, Atmos. Chem. Phys., 8, 1577–1590, doi:10.5194/acp-8-1577-2008, 2008.

Brooks, P. D. and Williams, M. W.: Snowpack controls on nitrogen cycling, Hydrol. Process., 13, 2177–2190, 1999.

Brooks, P. D., Williams, M. W., and Schmidt, S. K.: Microbial activity under alpine snowpacks, Biogeochemistry 32, 93–113, 1996.

Brooks, P. D., Schmidt, S. K., and Williams, M. W.: Winter production of CO_2 and N_2O from alpine tundra: environmental controls and relationship to inter-system C and N fluxes, Oecologia, 110, 403–413, 1997.

Caine, N.: Snowpack Influences on Geomorphic Processes in Green Lakes Valley, Colorado Front Range, The Geographical Journal, 161, 55–68, 1995.

Caine, N.: Streamflow patterns in the alpine environment of North Boulder Creek, ColoradoFront Range, Geomorphol., 1, 27–42, 1996.

Caine, N.: Recent hydrologic change in a Colorado alpine basin: an indicator of permafrost thaw? Annals of Glaciology, 51, 130–134, 2011.

Chin, Y., Traina, S. J., Swank, C. R., and Backhus, D.: Abundance and Properties of Dissolved Organic Matter in Pore Waters of a Freshwater Wetland, Limnol. Oceanogr., 43, 1287–1296, 1998.

Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, Mar. Chem., 51, 325–346, 1996.

Coble, P. G.: Marine Optical Biogeochemistry: The Chemistry of Ocean Color, Chem. Rev. 107, 402–418, 2007.

Darcy, J. L., Lynch, R. C., King, A. J., Robeson, M. S., and Schmidt, S. K.: Global distribution of Polaromonas phylotypes - evidence for a highly successful dispersal capacity, PLoS ONE, 6(8), e23742, doi:10.1371/journal.pone.0023742, 2011.

Darrouzet-Nardi, A., Erbland, J., Bowman, W. D., Savarino, J., and Williams, M. W.: Landscape-level nitrogen import and export in an ecosystem with complex terrain, Colorado Front Range, Biogeochemistry, doi:10.1007/s10533-011-9625-8, 2011.

de Wit, H. A., Hindar, A., and Hole, L.: Winter climate affects long-term trends in stream water nitrate in acid-sensitive catchments in southern Norway, Hydrol. Earth Syst. Sci. Discuss., 4, 3055–3085, doi:10.5194/hessd-4-3055-2007, 2007.

Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resources Laboratory, Silver Spring, MD, 2003.

Doskey, P. V. and Ugoagwu, B. J.: Atmospheric deposition of macronutrients by pollen at a semi-remote site in northern Wisconsin, Atmos. Environ., 23, 12, 2761–2766, 1989.

Economu, C. and Mihalopoulos, N.: Formaldehyde in the rainwater in the eastern Mediterranean: occurrence, deposition and contribution to organic carbon budget, Atmos. Environ., 36, 1337–1347, 2002.

Elser, J. J., Andersen, T., Baron, J. S., Bergström, A., Jansson, M., Kyle, M., Nydick, K. R., Steger, L., and Hessen, D. O.: Shifts in Lake N:P Stoichiometry and Nutrient Limitation Driven by Atmospheric Nitrogen Deposition, Science, 326, 5954, doi:10.1126/science.1176199, 2009.

Erickson, T., Williams, M. W., and Winstral, A.: Persistence of topographic controls on the spatial distribution of snow depth in rugged mountain terrain, Colorado, USA, Water Resour. Res., 41, W04014, doi:10.1029/2003WR002973, 2005.

Fellman, J. B., D'Amore, D. V., Hood , E., and Boone, R. D.: Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska, Biogeochemistry, 88,169–184, doi:10.1007/s10533-008-9203-x, 2009.

Freeman, K. R., Martin, A. P., Karki, D., Lynch, R. C., Mitter, M. S., Meyer, A. F., Longcore, J. E., Simmons, D. R., and Schmidt, S. K.: Evidence that chytrids dominate fungal communities in high-elevation soils, Proc. Natl. Acad. Sci., 106, 18315–18320, 2009a.

Freeman, K. R., Pescador, M. Y., Reed, S. C., Costello, E. K., Robeson, M. S., and Schmidt,

S. K.: Soil CO2 flux and photoautotrophic community composition in high-elevation, "barren" soils, Environ. Microbiol., 11, 674–686, 2009b.

Graber, E. R. and Rudich, Y.: Atmospheric HULIS: How humic-like are they? A comprehensive and critical review, Atmos. Chem. Phys., 6, 729–753, doi:10.5194/acp-6-729-2006, 2006.

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnol. Oceanogr., 53, 955–969, 2008.

IPCC: Climate Change 2007: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Parry, M. L., Canziani, O. F., Palutikof, J. P., van der Linden, P. J., and Hanson, C. E., Cambridge University Press, Cambridge, UK, 976 pp., 2007.

Jacobson, M. C., Hansson, H. C., Noone, K. J., and Charlson, R. J.: Organic atmospheric aerosols: review and state of the science, Reviews of Geophysics, 38, 267–294, 2000.

Jurado, E., Dachs, J., Duarte, C. M., and Simo, R.: Atmospheric deposition of organic and black carbon to the global oceans, Atmos. Environ., 42, 7931–7939, 2008.

Kieber, R. J., Peake, B., Willey, J. D., and Avery, G. B.: Dissolved organic carbon and organic acids in coastal New Zealand rainwater, Atmos. Environ., 36, 3557–3563, 2002.

Kieber, R. J., Whitehead, R. F., Reid, S. N., Willey, J. D., and Seaton, P. J.: Chromophoric dissolved organic matter (CDOM) in rainwater, southeastern North Carolina, USA, J. Atmos. Chem., 54, 21–41, doi:10.1007/s10874-005-9008-4, 2006.

Kieber, R. J., Willey, J. D., Whitehead, R. F., and Reid, S. N.: Photobleaching of chromophoric dissolved organic matter (CDOM) in rainwater, J. Atmos. Chem., 58, 219–235, 2007.

King, A. J., Meyer, A. F., and Schmidt, S. K.: High levels of microbial biomass and activity in unvegetated tropical and temperate alpine soils, Soil Biol. Biochem., 40, 2605–2610, 2008.

Kiss, G., Tomb'acz, E., Varga, B., Alsberg, T., and Persson, L.: Estimation of the average molecular weight of humic-like substances isolated from fine atmospheric aerosol, Atmos. Environ., 37, 3783–3794, 2003.

Lakowicz, J. R.: Principles of fluorescence spectroscopy, 3rd Edn. Springer, New York, USA, 2006.

Lawrence, C. R. and Neff, J. C.: The physical and chemical flux of eolian dust across the landscape: A synthesis of observations and an evaluation of spatial patterns, Chem. Geol., doi:10.1016/j.chemgeo.2009.02.005, 2009.

Lawrence, C. R., Neff, J. C., Painter, T., and Landry, C.: Contemporary composition of Aeolian dust deposited in the San Juan Mountains, Colorado, USA, J. Geophys. Res-Biogeo., 115, GO3007, doi:10.1029/2009JG001077, 2010.

Levin, E. J. T., Kreidenweis, S. M., McMeeking, G. R., Carrico, C. M., Collett Jr., J. L., and Malm, W. C.: Aerosol physical, chemical and optical properties during the Rocky Mountain Airborne Nitrogen and Sulfur study, Atmos. Environ., 43, 1932–1939, 2009.

Ley, R., Williams, M. W., and Schmidt, S.: Microbial population dynamics in an extreme environment: controlling factors in talus soils at 3750 m in the Colorado Rocky Mountains, Biogeochemistry, 68, 297–311, 2004.

Litaor M. I.: The influence of eolian dust on the genesis of alpine soils in the Front Range, Colorado, Soil Sci. Soc. Am. J., 51, 142–147, 1987.

Maie, N., Watanabe, A., and Kimura, M.: Chemical characteristics and potential source of fulvic acids leached from the plow layer of paddy soil, Geoderma, 120, 309–323, 2004.

Malm, W. C., Schichtel, B. A., Barna, M. G., Gebhart, K. A., Collett, J. L., and Carrico, C. M.: Source apportionment of sulfur and nitrogen species at Rocky Mountain National Park using modeled conservative tracer releases and tracers of opportunity, in: Proceedings of the 29th Conf. on Agricultural and Forest Meteorology/19th Symposium on Boundary Layers and Turbulence/Ninth Symp. on the Urban Environment, Keystone, CO, 1-6 August 2010.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T.: Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol. Oceanogr., 46, 38–48, 2001.

Meidute, S., Demoling, F., Baath, E.: Antagonistic and synergistic effects of fungal and bacterial growth in soil after adding different carbon and nitrogen sources, Soil Biol. Biochem., 40, 2334–2343, 2008.

Mitchell, B. G., Kahru, M., Wieland, J., and Stramska, M.: Determination of spectral absorption coefficients of particles, dissolved material and phytoplankton for discrete water samples, in: Ocean optics protocols for satellite ocean color sensor validation, Revision 4, Vol. IV, edited by: Mueller, J. L., Fargion, G. S., and McClain, C. R., NASA/TM-2003-211621/R, Goddard Space Flight Center, Greenbelt, Md., 39–56, 2003.

Mladenov, N., López -Ramos, J., McKnight, D. M., and Reche, I.: Alpine lake optical properties as sentinels of dust deposition and global change, Limnol. Oceanogr., 54, 2386–2400, 2009.

Mladenov, N., Reche, I., Olmo-Reyes, F. J., Lyamani, H., and Alados-Arboledas, L.: Relationships between spectroscopic properties of high altitude organic aerosols and sun photometry from ground-based remote sensing, J. Geophys. Res.-Biogeo., 115, G00F11,

doi:10.1029/2009JG000991, 2010.

Mladenov, N., Sommaruga, R., Morales-Baquero, R., Camarero, L., Laurion, I., Diéguez, M. C., Camacho, A., Delgado, A., Torres, O., Chen, X., Felip, M., and Reche, I.: Dusty skies, UV radiation, and bacteria influence organic matter concentration and optical quality in alpine lakes, Nature Comm., 2, 405, doi:10.1038/ncomms1411, 2011.

Morales-Baquero, R., Pulido-Villena, E., and Reche, I.: Atmospheric inputs of phosphorus and nitrogen to the southwest Mediterranean region: Biogeochemical responses of high mountain lakes, Limnol. Oceanogr., 51, 830–837, 2006.

Morris, D. P., Zagarese, H., Williamson, C. E., Balseiro, E. G., Hargreaves, B. R., Modenutti, B., Moeller, R., and Queimalinos, C.: The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon, Limnol. Oceanogr., 40, 1381–1391, 1995.

Muller, C., Baker, A., Hutchinson, R., Fairchild, I. J., and Kidd, C.: Analysis of rainwater dissolved organic carbon compounds using fluorescence spectrophotometry, Atm. Environ., 42, 8036–8045, 2008.

Neff, J. C., Ballantyne, A. P., Farmer, G. L., Mahowald, N. M., Conroy, J. L., Landry, C. C., Overpeck, J. T., Painter, T. H., Lawrence, C. R., and Reynolds, R. L.: Increasing eolian dust deposition in the western United States linked to human activity, Nature Geosci., 1, 189–195, doi:10.1038/ngeo133, 2008.

Nemergut, D. R., Anderson, S. P., Cleveland, C. C., Martin, A. P., Miller, A. E., Seimon, A., and Schmidt, S. K.: Microbial community succession in unvegetated, recently-deglaciated soils, Micro. Ecol., 53, 110–122, 2007.

Prenni, A. J., Petters, M. D., Kreidenweis, S. M., Heald, C. L., Martin, S. T., Artaxo, P., Garland, R. M., Wollny, A. G., and Pöschl, U.: Relative roles of biogenic emissions and Saharan dust as ice nuclei in the Amazon basin, Nat. Geosci., 2, 402–405, doi:10.1038/NGEO517, 2009.

Psenner, R.: Living in a dusty world: airborne dust as a key factor for alpine lakes, Water Air Soil Pollut., 112, 217–227, 1999.

Pulido-Villena, E., Reche, I., and Morales-Baquero, R. : Significance of atmospheric inputs of calcium over the southwestern Mediterranean region: High mountain lakes as tools for detection, Global Biogeochem. Cy., 20, GB2012, doi:10.1029/2005GB002662, 2006.

Reche, I., Ortega-Retuerta, E., Romera, O., Pulido-Villena, E., Morales-Baquero, R., and Casamayor, E. O.: Effect of Saharan dust inputs on bacterial activity and community composition in Mediterranean lakes and reservoirs, Limnol. Oceanogr., 54, 869–879, 2009.

Rhoades, C., Elder, K., and Greene, E.: The Influence of an Extensive Dust Event on Snow

Chemistry in the Southern Rocky Mountains, Arct. Antarct. Alp. Res., 42, 98–105, 2010.

Rogora, M.: Synchronous trends in N–NO3 export from N-saturated river catchments in relation to climate, Biogeochemistry, 86, 251–268, 2007.

Schmidt, S. K., Reed, S. C., Nemergut, D. R., Grandy, A. S., Cleveland, C. C., Costello, E. K., Weintraub, M. N., Hill, A. W., Meyer, A. F., Martin, A. P., and Neff, J. C.: The earliest stages of ecosystem succession in high-elevation (5000 meters above sea level), recently de-glaciated soils, Proc. Roy. Soc. B, 275, 2793–2802, doi:10.1098/rspb.2008.0808, 2008.

Schmidt, S. K., Nemergut, D. R., Miller, A. E., Freeman, K. R., King, A. J., and Seimon, A.: Microbial activity and diversity during extreme freeze-thaw cycles in periglacial soils, 5400 m elevation, Cordillera Vilcanota, Perú, Extremophiles, 13, 807–816, doi:10.1007/s00792-009-0268-9, 2009.

Sickman, J. O., Leydecker, A. L., Chang, C. C. Y., and Kendall, C.: Mechanisms underlying export of N from high-elevation catchments during seasonal transitions, Biogeochemistry, 64, 1–24, doi:10.1023/A:1024928317057, 2003.

Scully, N. M., Maie, N., Dailey, S. K., Boyer, J. N., Jones, R. D., and Jaffe, R.: Early diagenesis of plant-derived dissolved organic matter along a wetland, mangrove, estuary ecotone, Limnol. Oceanogr., 49, 1667–1678, 2004.

Sobek, S., Tranvik, L. J., Prairie, Y. T., Kortelainen, P., and Cole, J. J.: Patterns and regulation of dissolved organic carbon: An analysis of 7500 widely distributed lakes, Limnol. Oceanogr., 52, 1208–1219, 2007.

Stedmon, C. A. and Bro, R.: Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial, Limnol. Oceanogr. Meth., 6, 572–579, 2008.

Stedmon, C. A., Markager, S., and Bro, R.: Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy, Mar. Chem., 82, 239–254, 2003.

Waiser, M. J. and Robarts, D.: Changes in composition and reactivity of allochthonous DOM in a prairie saline lake, Limnol. Oceanogr., 45, 763–774, 2000.

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and Mopper K.: Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon, Environ. Sci. Technol., 37, 4702–4708, 2003.

Willey, J. D., Kieber, R. J., Eyman, M. S., and Avery Jr., G. B.: Rainwater dissolved organic carbon: concentrations and global flux, Global Biogeochem. Cy., 14, 139–148, 2000.

Williams, M. W. and Tonnessen, K. A.: Critical loads for inorganic nitrogen deposition in the

Colorado Front Range, USA, Ecol. Appl., 10, 1648–1665, 2000.

Williams, M. W. and Caine, N.: Hydrology and hydrochemistry, in: Alpine Dynamics: The Structure and Function of an Alpine Ecosystem: Niwot Ridge, Colorado, Oxford University Press, Oxford, England, 75–98, 2001.

Williams, M. W., Tonnessen, K., Melack, J., and Yang D.: Sources and spatial variation of the solute content of snow in the Tien Shan, PR China, Ann. Glaciol., 16, 25–32, 1992.

Williams, M. W., Baron, J., Caine, N., Sommerfeld, R., and Sanford, R.: Nitrogen saturation in the Colorado Front Range, Environ. Sci. Technol., 30, 640–646, 1996.

Williams, M. W., Davinroy, T., and Brooks, P. D.: Organic and inorganic nitrogen pools in talus soils and water, Green Lakes Valley, Colorado Front Range, Hydrol. Process., 11, 13, 1747–1760, 1997.

Williams, M. W., Cline, D., Hartmann, M., and Bardsley, T.: Data for snowmelt model development, calibration, and verification at an alpine site, Colorado Front Range, Water Resour. Res., 35, 10, 3205–3209, 1999.

Williams, M. W., Hood, E., and Caine, N.: The role of organic nitrogen in the nitrogen cycle of a high-elevation catchment, Colorado Front Range, USA, Water Resour. Res., 37, 10, 2569–2582, 2001.

Williams, M. W., Knauf, M., Cory, R., Caine, N., and Liu, F. J.: Nitrate content and potential microbial signature of rock glacier outflow, Colorado Front Range, Earth Surf. Proc., 32, 1032–1047, doi:10.1002/esp.1455, 2007.

Williams M. W., Seibold, C., and Chowanski, K.: Storage and Release of Solutes from a Subalpine Seasonal Snowpack: Soil and Stream Water Response, Niwot Ridge, Colorado, Biogeochemistry, 95, 77–94, doi:10.1007/s10533-009-9288-x, 2009.

Williams, M. W., Barnes, R. T., Parman, J. N., Freppaz, M., and Hood, E.: Stream Water Chemistry along an Elevational Gradient from the Continental Divide to the Foothills of the Rocky Mountains, Vadose Zone J., 10, 900–914, doi:10.2136/vzj2010.0131, 2011.

Wolford, R. A., Bales, R. C., and Sarooshian, S.: Development of a Hydrochemical Model for Seasonally Snow-Covered Alpine Watersheds: Application to Emerald Lake Watershed, Sierra Nevada, California, Water Resour. Res., 32, 1061–1074, 1996.

Wolfe, A. P., Baron, J. S., and Cornett, R. J.: Anthropogenic nitrogen deposition induces rapid ecological changes in alpine lakes of the Colorado Front Range (USA), J. Paleolimnol., 25, 1, 1–7, doi:10.1023/A:1008129509322, 2001.

Samburova, V., Zenobi, R., and Kalberer, M.: Characterization of high molecular weight compounds in urban atmospheric particles, Atmos. Chem. Phys., 5, 2163–2170, doi:10.5194/acp-5-2163-2005, 2005

Zhang, Q. and Anastasio, C.: Free and combined amino compounds in atmospheric fine particles (PM2.5) and fog waters from Northern California, Atmos. Environ., 37, 2247–2258, 2003.

Table 1. Volume weighted mean concentrations (C_{VWM})*, areal ~~loadings~~ (in kg ha^{-1}) of DOC and nutrients** ~~in wet deposition~~ at the Soddie collector, and DOC and nutrient loadings (in kg) to the 225 ha Green Lake 4 (GL4) catchment.

			DOC			TDN			TDP			Ca^{2+}	
Year	Precip (cm)	C_{VWM}	Areal ldg	Ldg to GL4	C_{VWM}	Areal ldg	Ldg to GL4	C_{VWM}	Areal ldg	Ldg to GL4	C_{VWM}	Areal ldg	Ldg to GL4
2002	48	1.19	5.7	1289	0.66	3.2	712	5.0	0.024	5	0.37	1.79	403
2003	46	1.41	6.5	1452	0.51	2.3	525	2.2	0.010	2	0.25	1.14	257
2004	81	0.77	6.2	1393	0.50	4.08	918	1.9	0.016	4	0.16	1.26	283
2005	113	1.12	12.6	2844	0.42	4.78	1075	2.2	0.025	6	0.19	2.12	476
2006	102	1.18	19.0	4276	0.57	5.9	1319	4.4	0.045	10	0.29	2.97	669
2007	85	0.94	8.1	1813	0.52	4.45	1001	3.9	0.033	7	0.21	1.79	403
2008	76	1.22	9.3	2098	0.43	3.25	731	2.8	0.022	5	0.33	2.50	562
2009	93	1.25	11.7	2628	0.35	3.25	731	5.2	0.049	11	0.40	3.72	836
2010	98	1.00	9.9	2220	0.29	2.83	637	4.4	0.043	10	0.68	6.7	1501
Mean	83	1.12	9.9	2224	0.47	3.78	850	3.57	0.030	7	0.32	2.7	599
δ	23	0.19	4.19	942	0.11	1.11	249	1.28	0.014	3	0.16	1.7	385

* All concentrations in mg L^{-1}, except for TDP (in µg L^{-1}).

* DOC = dissolved organic carbon; TDN = total dissolved nitrogen; TDP = total dissolved phosphorus; Ca^{2+} = calcium.

Table 2. Volume weighted mean concentrations (C_{VWM})* and yields (in kg) of DOC and nutrients** from Green Lake 4 (GL4)[a] and comparisons of wet deposition ~~loading~~ to lake yield.

Year	C_{VWM}	DOC Yield	~~loading~~: yield	C_{VWM}	TDN Yield	loading: yield	C_{VWM}	TDP Yield	loading: yield	C_{VWM}	Ca2+ Yield	loading: yield
2002	0.95	1492	0.86	0.29	329	2.16	2.2			2.81	4409	0.09
2003	0.92	2200	0.66	0.31	1057	0.50	3.9			2.21	5284	0.05
2004	0.96	1907	0.73	0.39	699	1.31	4.0			2.48	4953	0.06
2005	0.95	2322	1.22	0.32	1000	1.08	3.8			1.83	4451	0.11
2006	1.02	2109	2.03	0.25	602	2.19	3.8	7.90	1.27	1.90	3935	0.17
2007	0.87	1786	1.02	0.35	613	1.63	1.8	3.65	2.04	2.21	4552	0.09
2008	1.15	2377	0.88	0.32	677	1.08	2.8	5.77	0.85	2.37	4893	0.11
2009	0.92	1861	1.41	0.29	568	1.29	0.0			2.15	4354	0.19
Mean	0.97	2007	1.10	0.31	693	1.40	2.79	5.77	1.38	2.25	4604	0.11
δ	0.09	300	0.45	0.04	236	0.57	1.41	2.13	0.60	0.31	421	0.05

[a] During ice-free period (mid-May to mid-Oct).

All concentrations in mg L^{-1}, except for TDP (in µg L^{-1}).

* DOC = dissolved organic carbon; TDN = total dissolved nitrogen; TDP = total dissolved phosphorus; Ca^{2+} = calcium

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Table 3. Mean snow depth, mean snow density, and snow water equivalent at maximum accumulation (mid-May).

Year	Mean snow depth* (cm)	Mean snow density** (g m^{-3})	SWE (m)
2002	123	0.427	0.53
2003	222	0.374	0.83
2004	132	0.446	0.59
2005	215	0.408	0.88
2006	154	0.444	0.68
2007	123	0.435	0.54
2008	141	0.409	0.58
2009	147	0.372	0.55
2010	214	0.327	0.70

*Average of >500 points in the Green Lake Valley.

* Average of >8 points (SSW, 006, 084, 085, 087, 088, GL4, GL5, ARK, and NAV sites) in the Green Lake Valley (Fig. 1).

Table 4. DOC and nutrient concentrations*, ~~areal loading~~ (in kg ha^{-1} yr^{-1}), and loading to the Green Lake 4 (GL4) catchment (in kg yr^{-1}) in snow at maximum accumulation.

	DOC			TDN			TDP			Ca^{2+}		
year	C_{ma}	Areal ldg	Ldg to GL4	C_{ma}	Areal ldg	Ldg to GL4	C_{ma}	Areal ldg	Ldg to GL4	C_{ma}	Areal ldg	Ldg to GL4
2002	0.72	3.8	851	0.306	1.6	362	0.0066	0.03	8	0.306	1.6	361
2003	0.34	2.8	635	0.207	1.7	387	0.0056	0.05	10	0.315	2.6	589
2004	0.60	3.5	792	0.264	1.5	346	0.0066	0.04	9	0.130	0.8	170
2005	0.36	3.2	712	0.259	2.3	512	0.0033	0.03	6	0.138	1.2	273
2006	0.89	6.1	1373	0.205	1.4	315	0.0059	0.04	9	0.400	2.7	615
2007	0.37	2.0	448	0.248	1.3	300	0.0041	0.02	5	0.150	0.8	181
2008	0.42	2.4	545	0.209	1.2	271	0.0036	0.02	5	0.310	1.8	402
2009	0.48	2.6	590	0.187	1.0	230	0.0058	0.03	7	0.427	2.3	525
2010	0.65	5.1	1153	0.248	2.0	439	0.0066	0.05	12	0.467	3.7	828
average	0.54	3.50	788	0.24	1.56	351	0.0053	0.03	8	0.29	1.95	438
std dev	0.19	1.33	299	0.04	0.38	87	0.0013	0.01	2	0.13	0.98	219

* Mean of solute concentrations in the snowpack at maximum accumulation (C_{ma}) at SSW, 006, 084, 085, 087, 088, GL4, GL5, ARK, and NAV sites and expressed in mg L^{-1}, except for TDP (in µg L^{-1}).

Table 5. Values used to calculate the annual dry deposition loadings of each solute, including water soluble (WS) and water insoluble (WIN) loadings, in the 225 ha Green Lake 4 catchment.

Parameter	DOC	DOC in 2006§	TDN	TDP	Ca^{2+}
$M_{max-snow}$ (kg ha^{-1})	3.5	6.1	1.6	0.04	2.0
(kg accumulated)*	788	1373	351	8	438
$M_{max-wet}$ (kg ha^{-1})	3.6	4.8	1.9	0.01	2.0
(kg accumulated)*	810	1080	419	2	461
$M_{max-dryWS}$ (kg ha^{-1})	0	1.3	0	0.02	0
(kg accumulated)	0	293	0	5	0
$M_{max-dryWIN}$ (kg ha^{-1})	1.0	N	0.2	0.02	–
(kg accumulated)	225	N	52	4	–
$M_{annual-wet}$:$M_{max-wet}$	2.8	4.0	2.0	2.7	1.3
$M_{annual-wet}$ (kg ha^{-1})	9.9	19	3.8	0.03	2.7
(kg yr^{-1})**	2228	4275	855	7	608
$M_{annual-dryWS}$ (kg ha^{-1})	0	5.2	0	0.07	0
(kg yr^{-1})	0	1158	0	15	0
$M_{annual-dryWIN}$ (kg ha^{-1})	2.8	N	0.5	0.05	–
(kg yr^{-1})	619	N	106	12	–

* Mean of 2002–2010 loadings measured between October (first snowfall) and mid-May of each year.

* Mean of annual wet deposition loading from 2002–2010.

§ High dust loading year.

N = Particulate content only measured from 2002–2004; data not available for 2006.

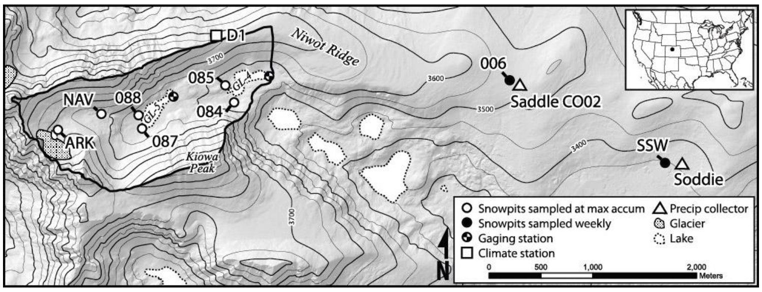

Fig. 1. Map of Niwot Ridge and the Green Lake 4 (GL4) catchment (outlined), showing Green Lake 4 (GL-4), the gaging station at GL-4, the D1 climate station, and sites of wet deposition (Saddle site NADP collector CO02 and Soddie site collector) and snow sampling. Inset shows the location of the Niwot Ridge LTER, Colorado, USA. ~~Art~~ credit: E. Parrish.

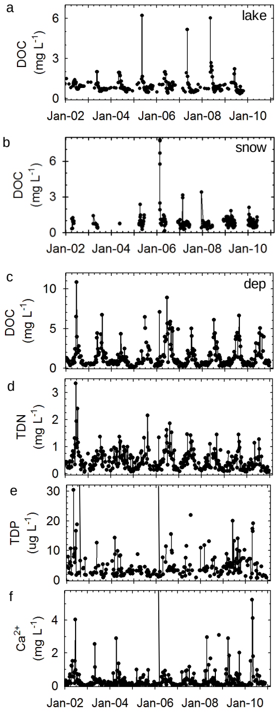

Fig. 2. Concentrations of **(a)** ~~dissolved organic carbon (~~DOC~~)~~ in Green Lake 4, **(b)** DOC in snow, and **(c)** DOC, **(d)** total dissolved nitrogen (TDN), **(e)** ~~total dissolved phosphorus (~~TDP~~)~~ and **(f)** ~~calcium (~~Ca^{2+}~~)~~ in wet deposition (dep). TDP and Ca^{2+} concentrations from 21 February 2006 were outside of the range shown on these figures, at 65 µg P L^{-1} and 10.5 mg Ca L^{-1}, respectively.

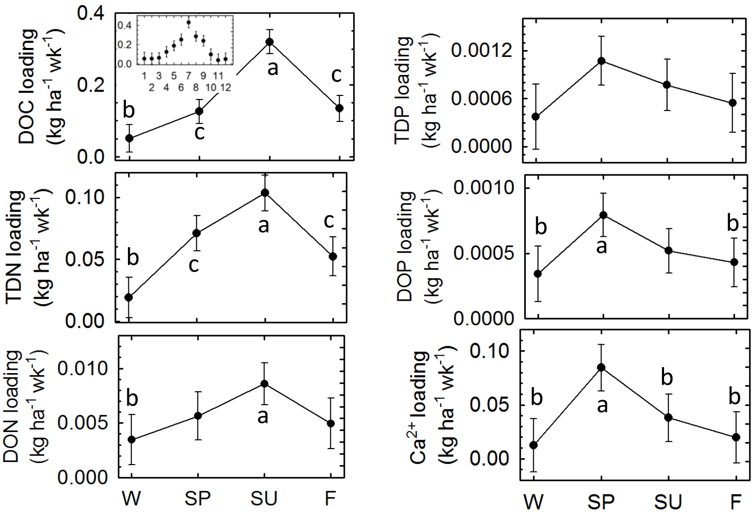

Fig. 3. Categorized means (by season; W = winter, SP = spring, SU = summer, F = fall) with 95 % confidence intervals for DOC, TDN, DON, TDP, DOP, and Ca^{2+} measured at Soddie from 2002–2010.Values that are significantly different from one another are denoted with different lowercase letters. Inset shows highest DOC loading during July (7th month).

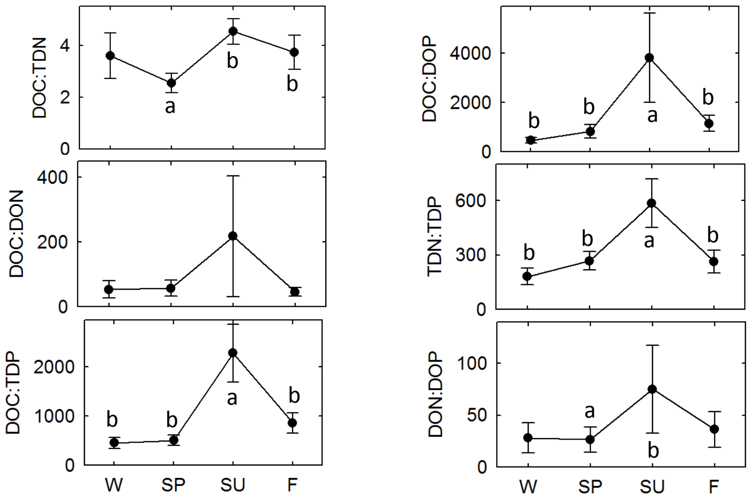

Fig. 4. Categorized means (by season; W = winter, SP = spring, SU = summer, F = fall) with 95 % confidence intervals for inorganic and organic C:N, C:P, and N:P ratios. Values that are significantly different from one another are denoted with different lowercase letters.

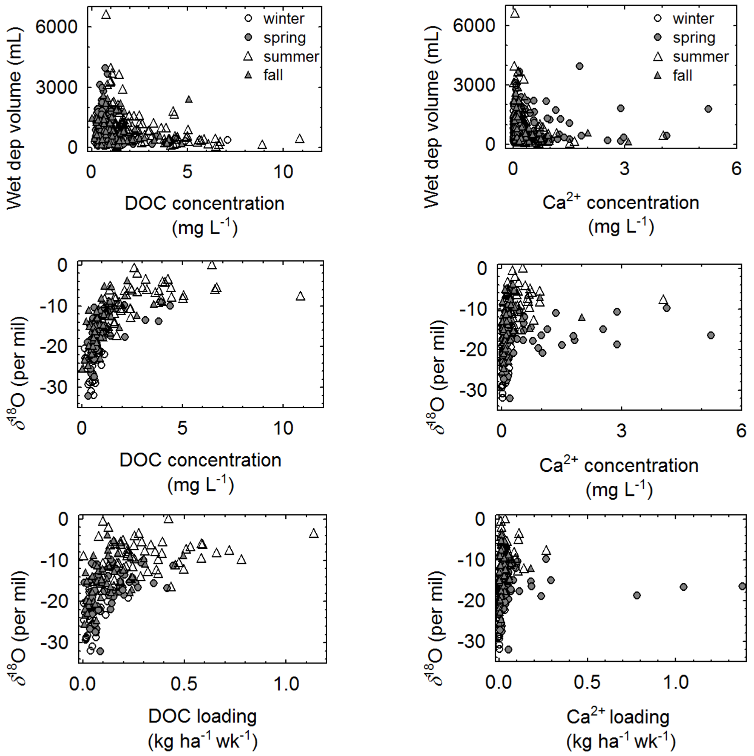

Fig. 5. DOC and Ca^{2+} concentrations and loadings at Soddie plotted agains the volume of wet deposition and stable isotopes of oxygen by season.

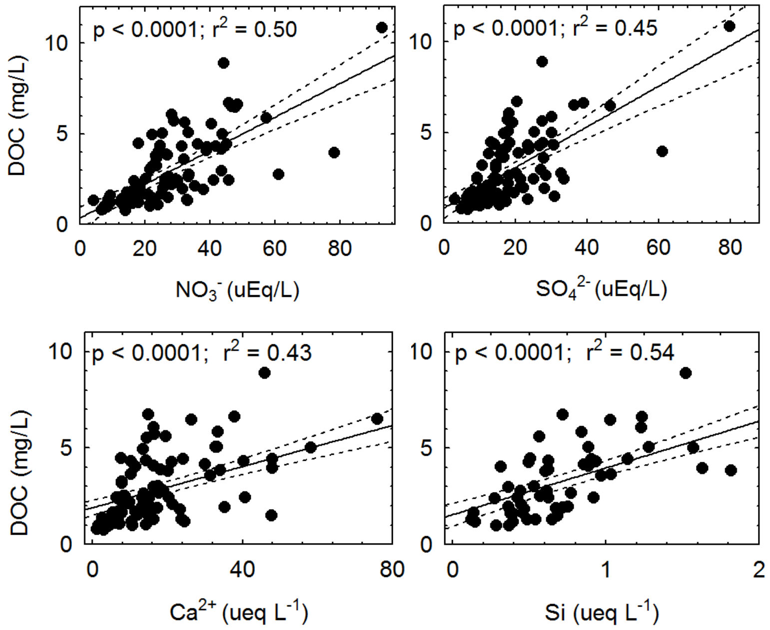

Fig. 6. Scatterplots of summer DOC concentration and **(a)** nitrate (NO_3^-), **(b)** sulfate (SO_4^{2-}), **(c)** calcium (Ca^{2+}), and **(d)** silica (Si^+) concentrations in wet deposition. Linear regressions with 95 % confidence intervals and significant relationships are shown.

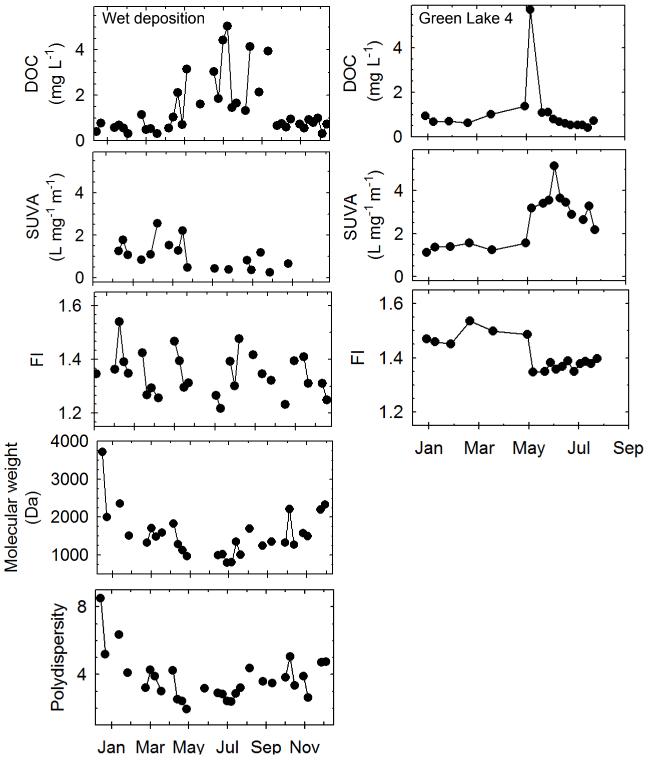

Fig. 7. Time series of DOC concentration, specific UV absorbance (SUVA), fluorescence index (FI), molecular weight, and polydispersity for 2010 wet deposition samples from the Soddie collector (left panels) and water samples from Green Lake 4 (right panels).

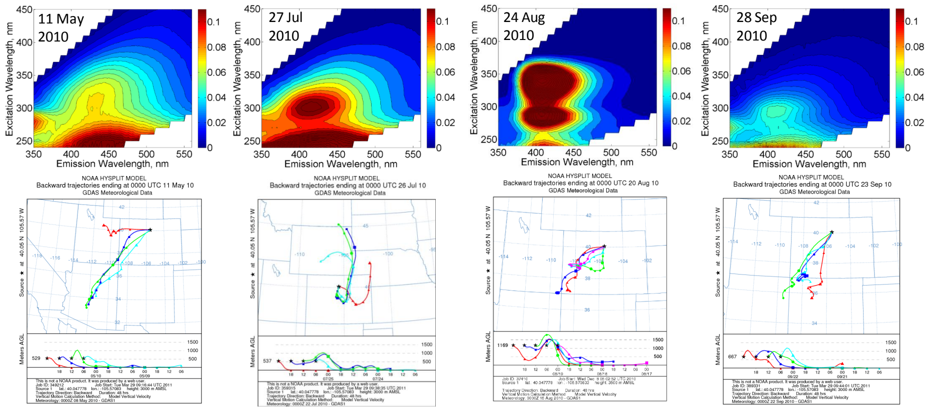

Fig. 8. Representative EEMs showing the diversity of fluorescence signatures from Soddie wet deposition. Samples collected on **(a)** 11 May 2010, **(b)** 27 July 2010, **(c)** 24 August 2010, and **(d)** 28 September 2010 are shown along with the corresponding 90 h backward trajectories taken at 6 h increments ending at 0000 UTC on the date during which precipitation was measured at the NADP gage (date is specified in each backward trajectory figure). Although most backward trajectories show the air masses have similar origin near the Colorado Plateau, each EEM is quite different. Corresponding DOC concentrations were 2.1 mg L^{-1}, 5.1 mg L^{-1}, 1.3 mg L^{-1}, and 4.0 mg L^{-1} for **(a)**, **(b)**, **(c)**, and **(d)** respectively. Corresponding Ca^{2+} concentrations were 4.1 mg L^{-1}, 0.66 mg L^{-1}, 0.12 mg L^{-1} and 0.24 mg L^{-1} for **(a)**, **(b)**, **(c)**, and **(d)** respectively. Corresponding TDN concentrations were 1.1 mg L^{-1}, 0.91 mg L^{-1}, 0.11 mg L^{-1} and 0.27 mg L^{-1} for **(a)**, **(b)**, **(c)**, and **(d)** respectively. Corresponding TDP concentrations were 16 µg L^{-1}, 0.8 µg L^{-1}, 0 µg L^{-1}, and 4.7 µg L^{-1} for **(a)**, **(b)**, **(c)**, and **(d)** respectively.

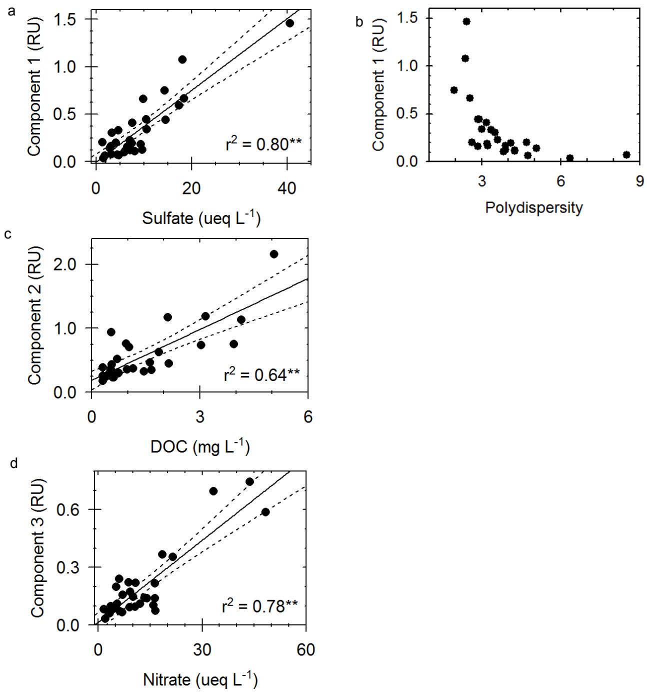

Fig. 9. Scatterplots of **(a)** fluorescent component 1 and sulfate concentration, **(b)** fluorescent component 1 and DOM polydispersity, **(c)** fluorescent component 2 and DOC concentration, and **(d)** fluorescent component 3 and nitrate concentration in wet deposition in 2010. Linear regressions with 95 % confidence intervals and significant relationships are shown.

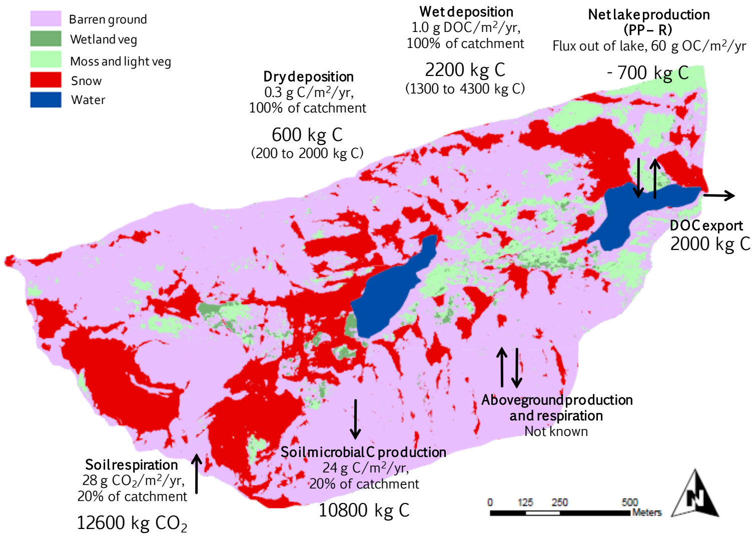

Fig. 10. Estimated annual C budget for the GL4 watershed overlaid on land classification map of June 2008. Only major pools are included. Wet and dry deposition mean values and ranges are derived from long term (2002–2010) weekly monitoring of wet deposition and snow at maximum accumulation. DOC export was taken as the mean annual yield from Green Lake 4. Other calculations are described in the Discussion. ~~Art and GIS credit: Erik Parrish, Boulder Creek CZO.~~