North-Watch Workshop

Potsdam, Germany

May 21-25, 2012

Hydrological Processes (In Press)

November 20, 2012

Title:

Lake-Watershed Sulfur Budgets and Their Response to Decreases in Atmospheric Sulfur Deposition:Watershed and Climate Controls

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ABSTRACT

Atmospheric sulfur (S) emissions peaked in North America in the early 1970s followed by declines in S deposition and sulfate (SO_4^{2-}) concentrations in surface waters. Changes in S biogeochemistry affect the mobilization of toxic (Al^{+3}, H^+) and nutrient (Ca^{2+}, Mg^{2+}, K^+) cations, and the acid-base status of ecosystems. We focused on lake/watersheds in the Adirondack Mountains of New York, USA, one of the most acid-sensitive and acid-impacted regions in North America. We used 16 of the 17 original Adirondack Long-Term Monitoring Lakes (ALTM) from 1984 through 2010 and found significant declines ($-2.14\ \mu mol_c\ L^{-1}\ yr^{-1}$) in SO_4^{2-} concentrations. There were significant declines (-0.28 kg S $ha^{-1}\ yr^{-1}$) in total S deposition for all lake/watersheds. We constructed S mass balances for 14 lakes/watersheds from wet and dry S deposition and SO_4^{2-} loss from drainage and found a comparable decline (-0.26 kg S $ha^{-1}\ yr^{-1}$) in lake SO_4^{2-} export. There was a discrepancy (mean 2.34 kg S $ha^{-1}\ yr^{-1}$) between atmospheric S deposition and watershed S loss due to internal S sources. Using major solute chemistry including dissolved silica and watershed characteristics, it was evident that the watershed S budget discrepancy increased with thickness of surficial deposits. The annual discrepancies in S mass balances were strongly linked with annual watershed discharge. These results suggest that internal S sources are becoming increasingly important as atmospheric S inputs have declined. The internal SO_4^{2-} supply of watersheds decreased concomitantly with lake acid neutralizing capacity (ANC). These findings suggest that the limited contributions from internal sources of SO_4^{2-} will facilitate the recovery of ANC from those lake/watersheds with the lowest ANC. With long-term decreases in atmospheric S deposition, the effects of climate, especially increases in precipitation, will play an increasingly important role in regulating S budgets and the amount of

SO_4^{2-} mobilized from internal watershed sources.

Keywords: Adirondack Mountains, Cations, Climate Change, Forested Watersheds, New York State, USA,

INTRODUCTION

Anthropogenic emissions of sulfur dioxide (SO_2) in Europe (Fowler et al., 2007; Vestreng et al. 2007) and North America (Lynch et al., 1996; Sickles and Shadwick, 2007; Weathers et al., 2006) have shown marked temporal changes over the past 100 years with peaks in the early 1980s and 1970s, respectively, followed by a marked decline (Figure 1). These declines in sulfur (S) emissions have resulted in decreases of the atmospheric S deposition and changes in surface waters draining forested watersheds including decreases in SO_4^{2-} concentrations and concomitant increases in pH and acid neutralizing capacity (ANC; Alewell et al., 2001; Driscoll et al., 2003; Mitchell et al., 2011; Mitchell and Likens, 2011; Prechtel et al., 2001; Stoddard et al., 1999, 2003). Within the United States there is strong regional variation in the atmospheric S deposition coinciding with spatial patterns of SO_2 emissions (Driscoll et al., 2001). Regional characteristics in bedrock and surficial geology and soils influence watershed sensitivity to acidic deposition. One of the regions that has been substantially impacted by atmospheric S deposition is the Adirondack Mountains in New York State, USA (Jenkins et al., 2007; Stoddard et al., 1999). The Adirondacks are largely forested (24,000 km^2). The Adirondacks are generally characterized by soils with low amounts of available nutrient cations (Sullivan et al., 2007) and a large number of lakes that have been acidified by acidic deposition (Driscoll et al., 1991, 2003, 2009).

A water monitoring program was established in 1982 to track concentrations of major solutes including sulfate from the outlets of 15 drainage and the surface of 2 seepage lake/watersheds (Driscoll and Van Dreason, 1993). Starting in 1993 the Adirondack Long Term Monitoring (ALTM) program was expanded to include an additional 35 sampling sites (total 52) to improve representation of classes of lake/watersheds across the Adirondacks. The ALTM has been used to evaluate chemical changes in the Adirondack surface waters (Driscoll et al., 2003). Details on the ALTM lake/watersheds can be found at: http://www.nyserda.ny.gov/Publications/Research-and-Development/Environmental.aspx. Previously, there have been efforts to develop lake/watershed element budgets using the ALTM lake chemistry. Ito et al. (2005a) estimated annual nitrogen (N) input-output budgets and dissolved organic carbon (DOC) losses for the 52 ALTM lake/watersheds for three years (1998 to 2000) using monthly N and DOC chemistry. Atmospheric inputs and hydrology were estimated using a combination of measured and modeled values. They found that both wet N deposition and watershed attributes affected the exports of nitrate (NO_3^-), ammonium (NH_4^+), dissolved organic nitrogen (DON) and DOC; the DOC/DON export ratio; and net N fluxes. Using a similar approach, Ito et al. (2005b) calculated mass balances of major ionic solutes in the ALTM lake/watersheds examining factors that affect the production of ANC. They found elevation was an important attribute controlling ANC production due to concomitant changes of biotic and abiotic processes along topographic gradients. Higher ANC associated with greater concentrations of base cations was found in lakes with thicker deposits of glacial till. In conjunction with field observations, the PnET-BGC model has been used to hindcast pre-industrial lake chemistry as well as to project potential future responses to decreases in atmospheric deposition (Chen and Driscoll, 2004ab; Chen et al., 2004; Zhai et al., 2008; Wu and Driscoll. 2009).

Mitchell et al. (2011) evaluated S budgets of 15 well-studied watersheds in the northeast United States and southeastern Canada including one ALTM lake/watershed (Arbutus Lake). This study provided an improved approach for estimating time series of total S deposition at various locations within the study region. Mitchell et al. (2011) found that most of the watersheds exhibited net losses of S from internal S soil sources. Such losses of S to drainage water may contribute to delays in the recovery of surface waters from the effects of acidic deposition (Church et al. 1989, 1992; Cosby et al. 1991). Mitchell et al. (2011) suggested that watershed wetness as quantified by annual surface water discharge has become an increasingly important driver of SO_4^{2-} loss in watersheds with decreases in atmospheric S deposition. This observation was further supported by a detailed evaluation of sulfur budgets at Hubbard Brook Experimental Forest in New Hampshire (U.S.A.) (Mitchell and Likens, 2011).

The objectives of this study were to evaluate: 1) long-term changes (1983-2010) in sulfur budgets in the original ALTM lake/watersheds; 2) temporal trends and spatial patterns in the sulfur budgets including an assessment of watershed characteristics that affect SO_4^{2-} loss, and 3) the role of internal sulfur sources in the recovery of these lake/watersheds from the effects of elevated acidic deposition.

METHODS

Study Lake/Watersheds

Characteristics of lake/watersheds used in this study are provided in Table 1 and locations are shown in Figure 2. For further details on the original ALTM lakes including lake surface area, lake volume, hydraulic retention time, vegetation cover, geology and surficial geology as well as information on analytical chemistry of water sampled see Driscoll and Van Dreason (1993). Note that the ALTM lake/watersheds have been classified by sensitivity to acidic deposition (Driscoll et al., 1991). This classification is largely based on hydrologic flowpaths and surficial geology. Ten of the lakes are located in the North Branch of the Moose River in the Adirondacks (Big Moose, Bubb, Cascade, Constable, Dart's, Moss, Rondaxe, Squash, West and Windfall; Driscoll and Newton, 1985; Driscoll et al., 1987). We focused on S dynamics from January 1984 through December 2010. The data set was generally complete with only a few missing values (<1% of all the data). Missing SO_4^{2-} concentrations were extrapolated by taking the mean concentration of those observations most close to the sampling dates before and after the missing value(s). Note that we also used volume-weighted concentrations of major solutes monitored in the ALTM program to interpret lake/watershed S budgets (see Driscoll and Van Dreason, 1993).

Measurements and Calculations of Components of the Lake/Watershed Budgets

Atmospheric Sulfur Deposition--The NADP/NTN data for the Huntington Wildlife Forest (NY20: http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=NY20) were used to determine average monthly concentrations of wet only precipitation from January 1984 through December 2010. Ito et al. (2002) developed empirical relationships for SO_4^{2-} concentrations of wet deposition within the Adirondacks based upon 23 deposition monitoring sites within and near the Adirondack Park using the following empirical equation:

$r^2 = 0.094$ and $p=0.034$

Concentration SO_4^{2-} mg L^{-1} = 15.2 + 0.440 * longitude -0.388 latitude + 0.00230*elevation;

Equation 1.

Using the following units:

Constant (mg L^{-1}); Longitude (mg L^{-1} deg^{-1}); Latitude (mg L^{-1} deg^{-1}); Elevation (m).

Dry S deposition was estimated using the formulations provided in Mitchell et al. (2011) where µg SO_2 m^{-3} was determined by:

Predicted = 0.9 + exp(7.867-0.463*Latitude + 0.149*Positive Longitude + 1.86e-07*total tons Eastern SO_2 emissions) Equation 2.

The data for SO_2 emissions were taken from the US EPA at:

http://ampd.epa.gov/ampd/

Comparison of predicted and observed concentrations of sulfur dioxide (SO_2) showed that the empirical relationships were able to reproduce estimates of dry S deposition: where y is the predicted and x represents the measured SO_2 concentrations:

$y=1.041x -223$, $r^2 = 0.882$ Equation 3

Using the calculated SO_2 concentrations, dry deposition values were estimated using the results from the CASTNET network by;

$\text{kg S ha}^{-1}\text{ yr}^{-1} = SO_2\ (\mu\text{g S m}^{-3}) * 1.17 + 0.00572\ (r^2 = 0.901).$ Equation 4

The annual dry S deposition values were calculated for each of the lake/watersheds over the period of lake chemistry time series.

Precipitation--Monthly precipitation amounts were obtained for the meteorological measurement station at Huntington Forest which is in close proximity to the Arbutus Lake/Watershed. These monthly precipitation amounts were extrapolated spatially to the other ALTM lake/watersheds using the empirical relationship developed by Ito et al. (2002) based upon 32 meteorological sites and normalized to the Huntington Forest. We used the following equation to calculate amounts of precipitation (cm) by month and among sites (r^2 =0.56, p=0.0002):

Monthly Precipitation = 22.7 + 7.09*Longitude – 10.4 Latitude + 0.0442 elevation Equation 5.

Using the following regression values and indicated units.

Constant (cm); Longitude (cm deg^{-1}); Latitude (cm deg^{-1}); Elevation (cm m^{-1}).

For each month and site sulfate (SO_4^{2-}) wet deposition was calculated by multiplying precipitation amount by precipitation SO_4^{2-} concentration.

Discharge--Information from the Arbutus Watershed was used to estimate discharge at the ALTM sites. For the period from 1984 through 1992, we used monthly modeled discharge as described in Mitchell et al. (1996), and for 1993 to 2010 we used measured values of discharge from the Arbutus Watershed. The Arbutus Watershed is the only ALTM lake/watershed with continuously monitored discharge. More details on the hydrology and biogeochemistry of this watershed located near the center of the Adirondacks can be found elsewhere (Mitchell et al., 2001; Park et al., 2003). To determine discharge at the other ALTM lake/watersheds, we calculated monthly discharge by scaling the discharge values obtained from the Arbutus Watershed based upon the precipitation estimates for the sites as described above with precipitation measured at the Huntington Forest (Ito et al., 2002). The monthly estimated discharge values for each lake/watershed were multiplied by their respective measured SO_4^{2-} concentrations to estimate SO_4^{2-} flux for each lake/watershed. To determine time-series trends in lake/watershed SO_4^{2-} concentrations, we used the non-parametric seasonal Kendall-Tau test (Hirsch and Slack, 1984).

Sulfur Budgets and Discrepancies--To determine annual (January - December) sulfur budgets for each lake watershed from 1984 through 2010, we summed monthly SO_4^{2-} precipitation amounts + annual dry S deposition and summed monthly estimates of SO_4^{2-} flux from discharge.

The S budget discrepancy is calculated on an annual basis as follows:

1) Wet and dry S atmospheric deposition determined on a yearly basis and expressed as kg S ha^{-1} yr^{-1};

2) S discharge determined on a yearly basis by summing monthly values and expressed as kg S ha^{-1} yr^{-1};

3) S deposition - S discharge = the difference in kg S ha^{-1} yr^{-1}; and

4) the difference in kg S ha^{-1} yr^{-1} is normalized by water flux in discharge by dividing this value by the volume of discharge in liters ha^{-1} yr^{-1} and with unit conversions can be expressed in µmol SO_4^{2-} L^{-1}. Temporal changes in the components of the lake/watershed S mass balances were evaluated by linear regression analysis (SAS, 2011).

RESULTS AND DISCUSSION

Sulfate Concentrations in Lake/Watershed Drainage Watersheds

All ALTM lake/watersheds showed significant declines in SO_4^{2-} concentrations over the study period (Table 2, Figure 3). The mean SO_4^{2-} decrease for all lakes was 2.14 μmol_c L^{-1} yr^{-1}, with a minimum rate of decrease of 0.96 μmol_c L^{-1} yr^{-1} for Barnes Lake (a seepage lake) and maximum rate of decrease of 2.86 μmol_c L^{-1} yr^{-1} for Constable Pond (a thin till drainage lake). The mean decrease in lake/watershed SO_4^{2-} concentrations for all of the drainage lakes was 2.23 μmol_c L^{-1} yr^{-1}. This rate of decrease is similar to the analyses provided for all of the original ALTM lakes by Driscoll et al. (2003) who found a significant ($p < 0.05$) and similar rates of decrease in SO_4^{2-} concentrations, with a mean rate of decline of 2.06 μmol_c L^{-1} yr^{-1} from 1982 to 2000. Comparable decreases in surface water SO_4^{2-} have been reported in previous studies (Stoddard et al., 1999) in southeastern Canada (e.g., Clair et al., 1995), northeastern U.S.A. (e.g, Driscoll et al., 1998) and Europe (e.g., Prechtel et al., 2001). These decreases in SO_4^{2-} concentrations reflect long-term decreases in atmospheric SO_2 emissions and total SO_4^{2-} deposition (Figure 1) as discussed below.

Lake/Watershed Sulfur Budgets

The mean (standard deviation) annual S deposition, SO_4^{2-} discharge and discrepancy in watershed S mass balance for all lake/watersheds were 8.45 (2.67), 10.8 (3.35) and -2.34 (2.62) kg S ha^{-1} yr^{-1}, respectively. For each drainage lake, watershed annual S budgets were constructed and budget discrepancies calculated as the difference between total atmospheric S inputs and drainage water SO_4^{2-} fluxes (Figure 4). Results for individual lake/watersheds should be interpreted with caution since we modeled important S budget components for most of the sites including S atmospheric deposition and water fluxes. Note, our project objective was to assess patterns in S inputs and losses across contrasting lake/watersheds of the Adirondacks. As such, we believe that given the number of lake/watersheds studied and given the length of the records, the approach used and the accuracy of the S mass balances are acceptable to reach broad conclusions about trends and the current state of S dynamics for the region. Moreover, the overall findings are compelling and consistent with analyses done at other sites in northeastern U.S. and southeastern Canada (Driscoll et al. 1998; Mitchell et al., 2011).

Atmospheric Deposition-- Squash and Black had the highest and lowest annual total S deposition 9.87 (2.87) and 5.72 (1.61) kg S ha^{-1} yr^{-1} respectively over the study period. Squash is located in the southwestern Adirondacks, an area characterized by high S deposition (Ito et al., 2002). In contrast Black is located in the northern Adirondacks, an area of relatively low S deposition (Ito et al., 2002).

Using linear regression, there were significant ($p<0.0001$, $n=378$) decreases in the mean total S deposition for all lake/watersheds over the study period (-0.28 kg S ha^{-1} yr^{-1}). There were also significant ($p<0.001$, $n=27$) decreases in total S deposition for all individual lake/watersheds with maximum and minimum changes of -0.32 and -0.18 kg S ha^{-1} yr^{-1} for Squash and Black, respectively.

Discharge--Sulfur discharge averaged 10.8 kg S ha^{-1} yr^{-1} for all sites and years combined. Among sites, the average (using all years) S discharge ranged from a maximum of 11.94 (3.20) for Otter and a minimum of 8.17 (2.39) kg S ha^{-1} yr^{-1} for Heart. Otter is located in the southern Adirondacks, while Heart is located in the northeastern Adirondacks and characterized by relatively low S deposition (Ito et al., 2002). There was a significant ($p<0.0001$, $n=378$) decrease in mean S discharge for all lake/watersheds (-0.26 kg S ha^{-1} yr^{-1}). There were also significant ($p<0.001$, $n=27$) decreases in S discharge for each individual lake/watershed with maximum and minimum changes of -0.32 and -0.19 kg S ha^{-1} yr^{-1} at Constable and Heart, respectively. The similarity between the long-term decreases in atmospheric S deposition and S discharge support the dominant role of decreases in atmospheric S inputs in driving long-term changes in the S budgets of forested watersheds and lakes in the Adirondacks.

Sulfur Budget Discrepancies--The average discrepancy in S mass balances for all lake/watersheds for all years studied was -2.34 kg S ha^{-1} yr^{-1}. The sites with the highest and lowest S budget discrepancies were -4.81 (2.44) for Arbutus and -0.42 (2.87) kg S ha^{-1} yr^{-1} for Squash, respectively. Previous work at the Arbutus Watershed using chemical and isotopic tracers has found for the major inlet (Archer Creek) there is evidence for a weathering source of

S to the watershed (Campbell et al., 2006; Piatek et al., 2009). Arbutus is medium till drainage lake/watershed with low dissolved organic carbon and relatively high ANC (> ~50 µmol$_c$ L^{-1} from 1983-2010. Squash has thin deposits of glacial till in the watershed and has relatively low ANC (0 to -50 µmol$_c$ L^{-1} from 1983-2010).

It is likely that the flux of S depicted as the discrepancy in S budget represents an internal source of S from the watershed. A portion of this S could be derived from weathering inputs, as has been documented for Arbutus Lake watershed (Campbell et al., 2006). Alternatively, the internal supply of watershed S could be due to net mineralization of organic S in soil or net desorption of SO_4^{2-} from soil surfaces. These latter two sources are the result of historical elevated atmospheric S deposition which was retained in the watershed. With decreases in S deposition, we would anticipate that these legacy deposits of atmospheric S deposition would be mobilized to drainage waters as the watershed approaches steady-state with respect to a new, lower atmospheric S deposition. We do not have specific information on which or what combination of these processes (S mineral weathering, net organic S mineralization, desorption of previously adsorbed SO_4^{2-}) is contributing to the discrepancy in lake/watershed S budgets. Previous research using stable S isotopes suggests that S inputs cycle through soil organic S before export as SO_4^{2-} in drainage water (Alewell et al., 1999; Gbondo-Tugbawa et al., 2002; Likens et al., 2002). Based on this previous research, we anticipate that net S mineralization and net SO_4^{2-} desorption to be the major sources of internal S supplied from most ALTM watersheds. However, we did not observe a significant or consistent long-term change in the discrepancy in lake/watershed S balance at any of the ALTM sites. The lack of a long-term trend in the discrepancy in watershed S budgets may be indicative of a weathering S source as the contributing process. If net soil S mineralization and/or desorption of SO_4^{2-} are contributing, we anticipate that the discrepancy in watershed S would decreases over time following decreases in atmospheric S deposition; however, this pattern is currently obscured by large year-to-year variation in climatic conditions(see below).

Effect of Discharge and Watershed Wetness on Sulfur Budgets

There was considerable interannual variation in lake/watershed S budgets for the Adirondacks that is strongly dependent on precipitation quantity and discharge. Examples are shown for Arbutus (Figure 5), Big Moose (Figure 6) and Squash (Figure 7), illustrating the range of inter-annual variation in S budget components, particularly S discharge and S discrepancies.

Previous work for watersheds throughout southeast Canada and the northeast United States (Mitchell et al., 2011) including a detailed investigation at the Hubbard Brook Experimental Forest in New Hampshire (USA) (Mitchell and Likens, 2011) suggests the importance of precipitation quantity and discharge as a metric of watershed wetness and an important driver of the discrepancy in watershed S budgets. There is a direct relationship between the amount of discharge and the amount of SO_4^{2-} exported from watersheds due to multiplicative effect of concentration and discharge in quantifying drainage flux. Hence it is useful to normalize the discrepancy in lake/watershed S balance on the basis of annual discharge and therefore express the discrepancy as annual volume-weighted S concentration as detailed in Mitchell et al. (2011) and Mitchell and Likens (2011). The discrepancy in lake/watershed S balance expressed as annual volume-weighted S concentrations for ALTM lake/watersheds ranged from -22.9 μmol_c

SO_4^{2-} L^{-1} (Arbutus) to -0.1 μmol_c SO_4^{2-} L^{-1} (West), with only Squash showing positive value of 1.2 μmol_c SO_4^{2-} L^{-1} (i.e., net SO_4^{2-} retention; Table 3). These values of discrepancy in lake/watershed S mass balance are within a narrower range than the S discrepancies (-42 to + 14 μmol_c SO_4^{2-} L^{-1}) found for watersheds throughout the broader region of southeastern Canada and the northeastern U.S. (Mitchell et al., 2011).

Combining the results for all ALTM lake/watersheds there was a strong relationship ($p<0.001$, $r^2=0.48$) between $\log_{10}$ annual discharge and the annual S budget discrepancies expressed as volume-weighted SO_4^{2-} concentration (Table 4 and Figure 8). For the individual watersheds ($p<0.001$, $r^2> 0.66$) the slopes of this relationship ranged from -107.1 (Squash) to - 76.1 (Black) μmol_c SO_4^{2-} $L^{-1}/\log_{10}$ discharge in cm yr^{-1}. Note that 2001 was exceptionally low in precipitation and hence in low discharge and resulted in a positive S budget discrepancy (expressed μmol_c SO_4^{2-} L^{-1}; Figure 8). The resultant effect of this dry year on annual S budgets are also evident in the three budgets we provided of annual mass S balances for individual lake/watersheds (Figures 4, 5 and 6). Conducting the regression analyses without 2001 values did not affect the significant relationships between discharge and S budget discrepancy. Watershed discharge could affect a number of chemical and biotic processes that could enhance SO_4^{2-} mobilization from forest soils and hence leaching into surface waters. These processes would include increased S mineralization from the organic S pool of forested soils (Mitchell et al., 1992) and desorption of SO_4^{2-} (Johnson and Mitchell, 1998), the former may be the more important process for forested soils in the study region (Mitchell et al., 2011; Gbondo-Tugbawa et al., 2002; Likens et al., 2002). Increased precipitation would also increase the wetted surface area of soil minerals and therefore potentially contribute to increases in S mineral weathering rates. Wetting and drying cycles can also result in SO_4^{2-} mobilization of previously reduced S (Eimers 2004abc, Kerr et al., 2012). Wetness also affects the connectivity of surface waters within watersheds to the contributing areas of various solute sources (Creed and Band, 1998; Inamdar et al., 2004). Hence increased watershed wetness and discharge would likely result in the enhanced SO_4^{2-} transport from soils to streams.

Landscape Factors Controlling Internal Watershed S Supply

We used ALTM water chemistry characteristics to gain insight on the watershed factors controlling the internal S supply (i.e., discrepancy in lake/watershed S balance) and to improve understanding of the role of this process for the recovery of Adirondack soils and lakes from acidification by acidic deposition. We observed several relationships that point to the importance of surficial geology and the associated inputs of groundwater from deeper surficial deposits as being an important controller of the internal SO_4^{2-} supply to ALTM lakes. Based on ALTM lake classes, we generally observed higher values for discrepancy in S balance for lakes/watersheds that are situated in thick and medium deposits of glacial till, than thin till sites (Table 1 and Figure 4). With the exception of Arbutus which has a substantial weathering source of S (Campbell et al. 2006), there is relatively strong relationship between discrepancy in lake/watershed S budgets and volume-weighted concentrations of dissolved silica (Si) in ALTM drainage lakes (Figure 8b; $r^2 = 0.31$, $p=0.04$ and $r^2 = 0.\ 0.60$, $p=0.001$ without Arbutus). Concentrations of dissolved Si from mineral weathering are a good measure of groundwater inputs and the associated supply of solutes, including SO_4^{2-}, to lakes from deeper surficial deposits (Chen et al. 1984; Peters and Driscoll 1987).

We observed that a large fraction of the spatial variation in the volume-weighted concentrations of SO_4^{2-} in ALTM drainage lakes, could be explained by the discrepancy in lake/watershed S budgets ($r^2 = 0.61$, p=0.0008 Figure 8a). Characterizing net mineralization of soil organic S and the net desorption of SO_4^{2-} is critical in quantifying the role of watershed processes in delaying the recovery of surface waters from acidification by acidic deposition (Driscoll et al. 1998, 2001). Our analysis from the ALTM lakes suggests that, if operating, these processes may be less important in delaying surface water recovery than previously thought. Excluding Arbutus, there is a relatively strong relationship of decreasing discrepancy in ALTM watershed S budgets with decreasing volume-weighted lake ANC (Figure 8c; r^2= 0.47, 0.008 and 0.53, p=0.003 without Arbutus). This pattern indicates that with increasing sensitivity to acidic deposition (low ANC) Adirondack lake/watersheds have a decreasing fraction of their watershed S budgets derived from internal watershed sources. As a result, the lakes which are most sensitive and have been most impacted by acidic deposition appear to be responding the most rapidly to decreases in atmospheric S deposition without experiencing substantial delays associated with the mobilization of legacy S from within the watersheds. Alternatively, if these discrepancies in lake/watershed S budgets are due to S mineral weathering, this process would not affect the recovery of Adirondack lakes (Driscoll et al., 1998).

Climate Change in the Adirondacks and Potential Impacts on Sulfur Budgets

The Adirondacks could face a 3 to 6 °C increase in temperature over the next 50-100 years, and possibly a 20% increase in overall annual precipitation (Frumhoff et al., 2007). Bier et al. (2012) observed decreasing periods of lake ice cover in the Adirondacks as evidence of climate change. Climate change is occurring over the entire northeast United States including the Adirondacks (Huntington et al., 2009) with important linkages to forest watershed hydrology and biogeochemistry (Campbell et al., 2009, 2011). A recent report has also provided supporting information derived from broad range of sources that indicate an increase in temperature and precipitation in the Adirondack region of New York State (Horton et al., 2011). We have shown the importance of discharge in controlling SO_4^{2-} losses from watersheds. With anticipated increases in precipitation quantity and decreases in atmospheric S deposition, we would expect lake/watershed S losses will be more variable in the future; less driven by atmospheric deposition and more driven by year to year climatic variation.

Implications for Watersheds in Other Regions

Our results suggest that further evaluation of watershed S budgets of other regions in North America, Europe and in Asia would provide insight on the responses to changes in atmospheric S deposition suggested in the study. Patterns of surface water SO_4^{2-} responses in well-studied watersheds could help in ascertain important factors affecting the dynamics of S budgets of individual watersheds as well as for regions. Both Europe (Fowler et al., 2007; Vestreng et al. 2007) and North America (Lynch et al., 1996; Sickles and Shadwick, 2007; Weathers et al., 2006) have shown marked declines in emissions of S and resultant atmospheric S deposition. The concomitant understanding of the influences of declining S deposition, watershed characteristics and climate change, especially the amount of precipitation, are needed to improve projections of the recovery of watersheds from acidification. Such information can be used to advance the determination of critical and target loads (Nilsson and Grennfelt, 1988; Sullivan et al., 2005, 2012; Vries 1993), and to amend watershed S algorithms in biogeochemical models (Chen and Driscoll, 2004ab; Wu and Driscoll. 2009) that predict long-term changes in watershed biogeochemistry.

CONCLUSIONS

We have developed sulfur budgets across lake/watersheds in the Adirondacks of New York State utilizing detailed information on hydrology, deposition and chemistry available from the Arbutus Watershed and the Huntington Wildlife Forest and long-term (1983-2010) lake chemistry information available from the Adirondack Long-Term Monitoring (ALTM) program (Driscoll and Van Dreason, 1993). We extrapolated precipitation quantity, atmospheric S deposition and watershed discharge using information from Mitchell et al. (2001 and 2011) and Ito et al. (2002). These results not only improve understanding S watershed budgets, but also provide insight on changes in the mobilization of SO_4^{2-} and the concomitant mobilization of toxic (Al^{+3}, H^+) and nutrient (Ca^{2+}, Mg^{2+}, K^+) cations in response to decreases in atmospheric S deposition (Johnson and Mitchell, 1998). Using the average annual volume-weighted concentration of sulfur budget discrepancy (-9.36 μmol_c SO_4^{2-} L^{-1}) and an average annual discharge rate (64.3 cm yr^{-1}) results in a mobilization of S from internal watershed sources of 2.34 kg S ha^{-1} yr^{-1}. This amount of internal S loss is increasing in importance in lake/watershed S budgets compared with current atmospheric S deposition, which has decreased to < 4 kg S ha^{-1} yr^{-1} (e.g. Figures 5-7). Internal sources are currently >50% of the S supplied from atmospheric deposition. Note the internal SO_4^{2-} supply of these lake/watersheds decreases concomitantly with lake acid neutralizing capacity (ANC) across the Adirondack lakes. This pattern suggests that the small contributions from internal legacy sources of S from past elevated atmospheric deposition will facilitate in the recovery from acidification in low ANC lakes. An increase in precipitation inputs due to climate change is predicted for this region and will likely play an increasingly important role in regulating watershed S budgets possibly increasing the amount of SO_4^{2-} mobilized from internal sources. The Adirondacks have been identified as one of the most acid-sensitive regions in North America (Driscoll et al., 1991) and even though there have been marked declines in S emissions and resultant deposition, the recovery of the Adirondacks surface waters has been relatively slow (Driscoll et al., 2003, 2009). Quantification of the changes and interactions of atmospheric deposition and climate affect watershed S biogeochemistry and resultant interactions with other solutes are needed to improve understanding lake/watershed responses to these important environmental changes.

ACKNOWLEDGEMENTS

This research was sponsored in part by the National Science Foundation (Ecosystem Studies), the Northeastern States Research Cooperative (NSRC), administered by the USDA Forest Service, and York State Energy Research and Development Authority (NYSERDA). The support of the Environmental Monitoring, Evaluation, and Protection (EMEP) of NYSERDA has been especially important in maintaining the deposition monitoring and watershed measurements at the Huntington Forest. Since 1993, the field collections and chemistry analysis for the ALTM are carried out by the Adirondack Lakes Survey Corporation which is supported NYSERDA, the New York State Department of Environmental Conservation Division of Air Resources and the U.S. Environmental Protection Agency. Steve Signell helped in preparing the figure showing site locations.

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LIST OF FIGURES

Table 1. Lake/watershed characteristics of the original Adirondack Lake Term Monitoring Lakes (ALTM). For more details see Driscoll and Van Dreason (1993).

Lake/Watershed Name	**Latitude** ° ‘	**Longitude** ° ‘	**Type**	**Till Type**	**Watershed area (ha)**	**Lake surface area (ha)**
Arbutus	43 58	74 14	drainage	Medium till	364.8	48.2
Barnes	43 34	75 14	seepage	Not applicable	6.5	2.9
Big Moose	43 49	74 51	drainage	Thin till	9584.6	512.5
Black	44 26	74 18	drainage	Thick till	344.2	29.0
Bubb	43 46	74 51	chain drainage	Thin till	185.8	18.2
Cascade	43 48	74 49	drainage	Medium till	474.8	40.4
Clear	43 59	74 50	drainage	Thin till	600.6	70.4
Constable	43 49	74 50	chain drainage	Thin till	945.1	20.6
Dart	43 48	74 53	chain drainage	Thin till	10756.5	51.8
Heart	44 26	74 18	drainage	Medium till	62.9	10.7
Little Echo	44 18	74 22	seepage	Not Applicable	7.3	0.8
Moss	43 46	74 51	drainage	Medium till	1314.7	45.7
Otter	43 11	74 30	chain drainage	Thin till	361.2	14.8
Rondaxe	43 45	74 55	chain drainage	Thin till	14282.9	90.5
Squash	43 49	74 53	drainage	Thin till	41.3	3.3
West	43 49	74 53	drainage	Thin till	108.1	10.4
Windfall	43 48	74 51	drainage	Carbonate Influenced	43.7	2.4

Table 2. Regression of lake/watershed sulfate concentration against time evaluated using the Mann-Kendall trend test.

Lake/watershed *Seepage	N	p value	slope $\mu mol_c\ L^{-1}\ year^{-1}$
Arbutus	327	<0.00001	-2.11
Barnes*	276	<0.00001	-0.96
Big Moose	339	<0.00001	-2.67
Black	336	<0.00001	-1.92
Bubb	339	<0.00001	-1.97
Cascade	339	<0.00001	-1.88
Constable	340	<0.00001	-2.86
Dart’s	340	<0.00001	-2.61
Heart	334	<0.00001	-1.80
Rondaxe	340	<0.00001	-2.35
Little Echo*	334	<0.00001	-1.50
Moss	339	<0.00001	-2.14
Otter	331	<0.00001	-2.17
Squash	323	<0.00001	-2.22
West	339	<0.00001	-2.53
Windfall	339	<0.00001	-2.61

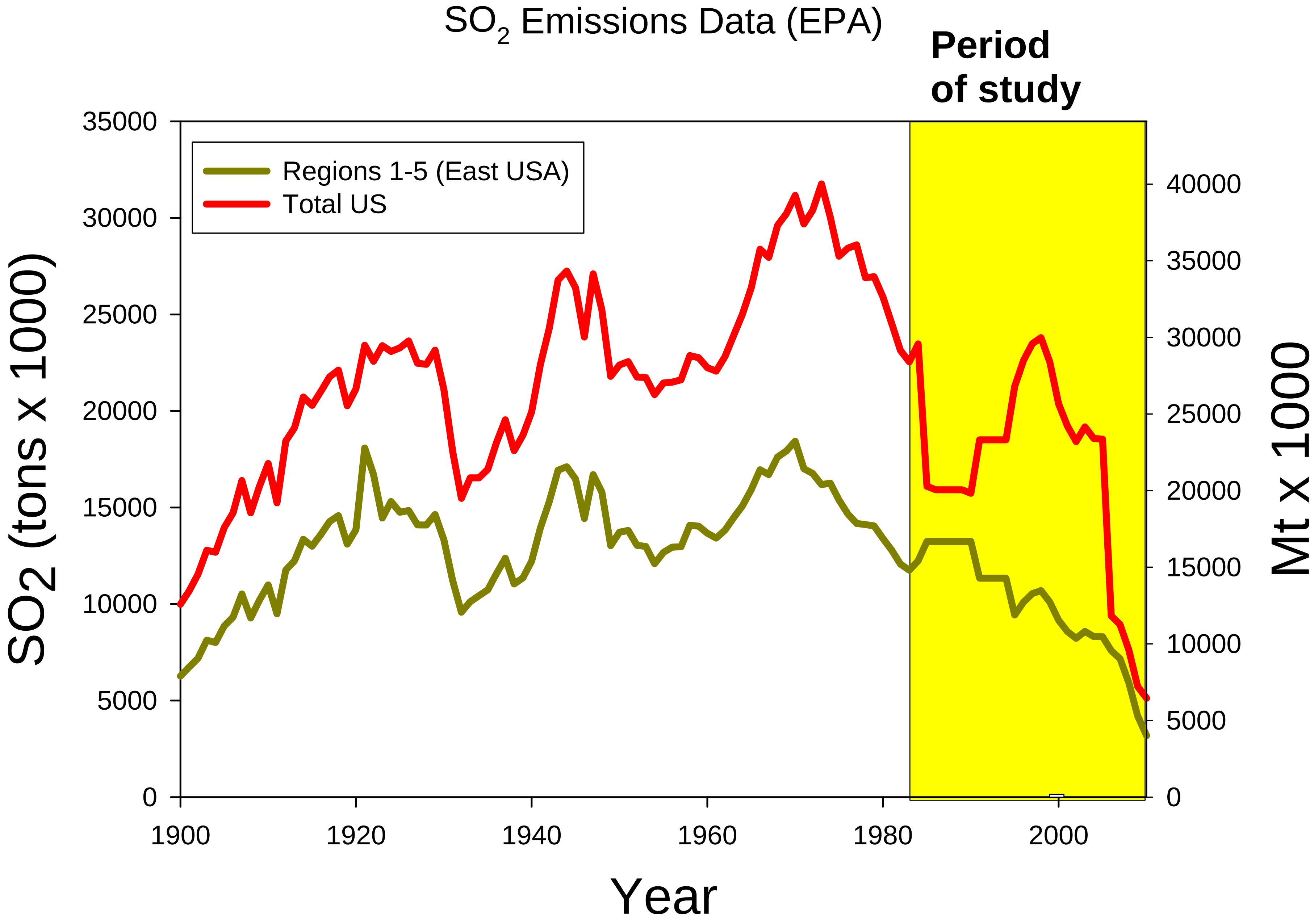
Table 3. Discrepancy as sulfate concentration normalized for discharge μmol$_c$ SO_4^{2-} L^{-1} (n= 27 years)

Lake/Watershed	Mean	Standard Deviation
Arbutus	-22.9	10.9
Big Moose	-8.3	13.4
Black	-20.1	10.1
Bubb	-4.4	14.7
Cascade	-11.2	12.8
Constable	-11.8	13.2
Dart	-8.1	13.3
Heart	-4.6	11.2
Lake	-7.6	13.6
Moss	-10.6	13.0
Otter	-9.4	14.3
Squash	1.1	14.6
West	-0.1	13.6
Windfall	-13.0	13.2

Table 4. Sulfur Budget Discrepancies in relationship to watershed wetness/discharge

Lake/Watershed	Slope (μmol_c SO_4^{2-} L^{-1} $\log_{10}$ annual discharge cm)	Intercept	r^2	p value
Arbutus	-80.67	129	0.689	<.0001
Big Moose	-102.5	176	0.740	<.0001
Black	-76.11	113	0.716	<.0001
Bubb	-105.7	186	0.665	<.0001
Cascade	-93.14	156	0.666	<.0001
Constable	-98.3	165	0.707	<.0001
Dart	-101.1	174	0.735	<.0001
Heart	-82.4	141	0.688	<.0001
Moss	-95.21	161	0.679	<.0001
Otter	-104	179	0.664	<.0001
Rondaxe	-101	174	0.704	<.0001
Squash	-107.1	196	0.683	<.0001
West	-100.5	181	0.692	<.0001
Windfall	-96.36	161	0.668	<.0001

Figure 1



SO₂ Emissions Data (EPA)
Period of study
Regions 1-5 (East USA)
Total US
35000
30000
25000
20000
15000
10000
5000
0
40000
35000
30000
25000
20000
15000
10000
5000
0
1900
1920
1940
1960
1980
2000
SO2 (tons x 1000)
Mt x 1000
Year

Figure 2

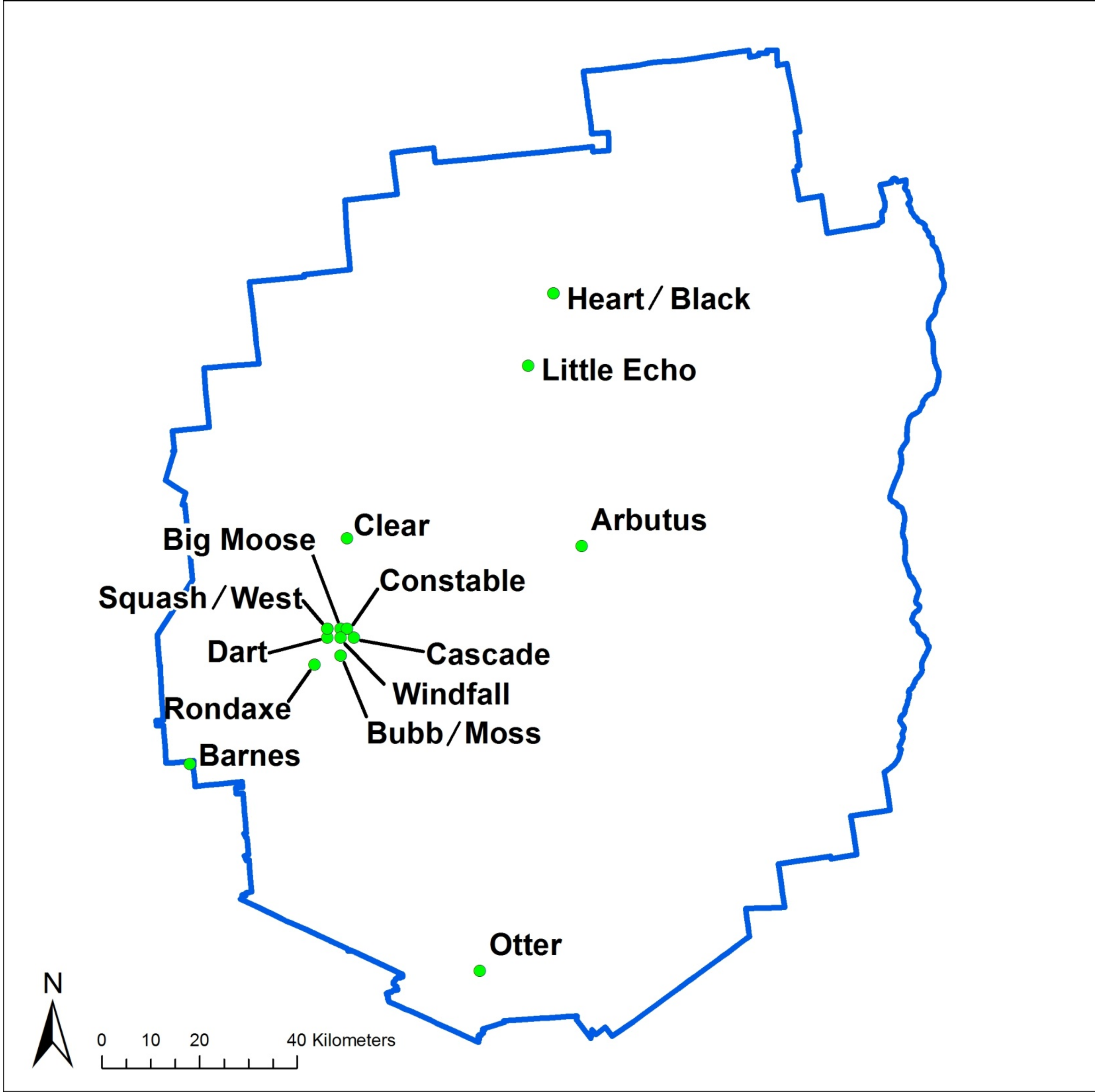

Heart / Black
Little Echo
Clear
Arbutus
Big Moose
Constable
Squash / West
Dart
Cascade
Windfall
Rondaxe
Bubb / Moss
Barnes
Otter
N
0
10
20
40 Kilometers

Figure 3.

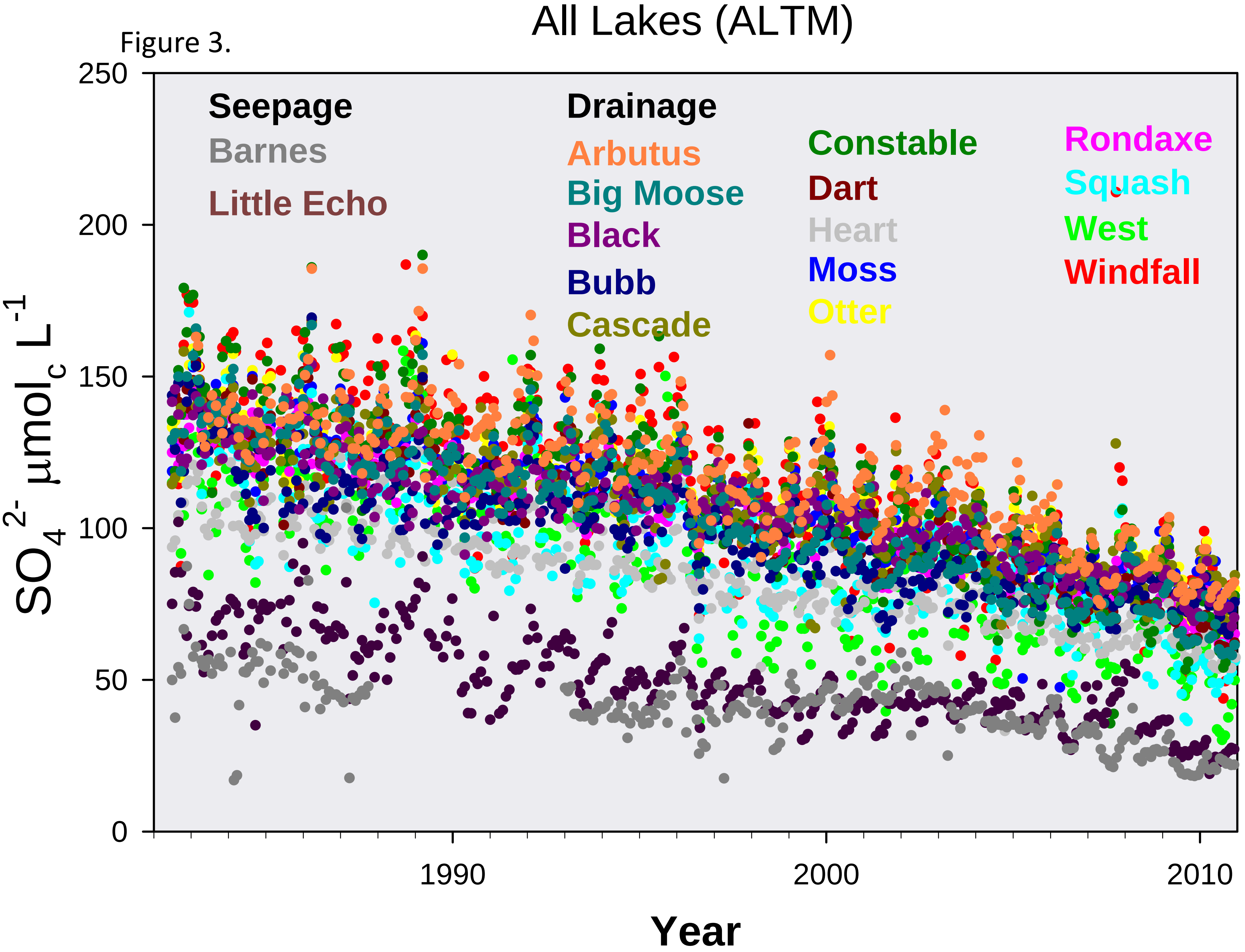

All Lakes (ALTM)
Seepage
Barnes
Little Echo
Drainage
Arbutus
Big Moose
Black
Bubb
Cascade
Constable
Dart
Heart
Moss
Otter
Rondaxe
Squash
West
Windfall
SO_4^{2-} µmol$_c$ L^{-1}
0
50
100
150
200
250
1990
2000
2010
Year

Figure 4

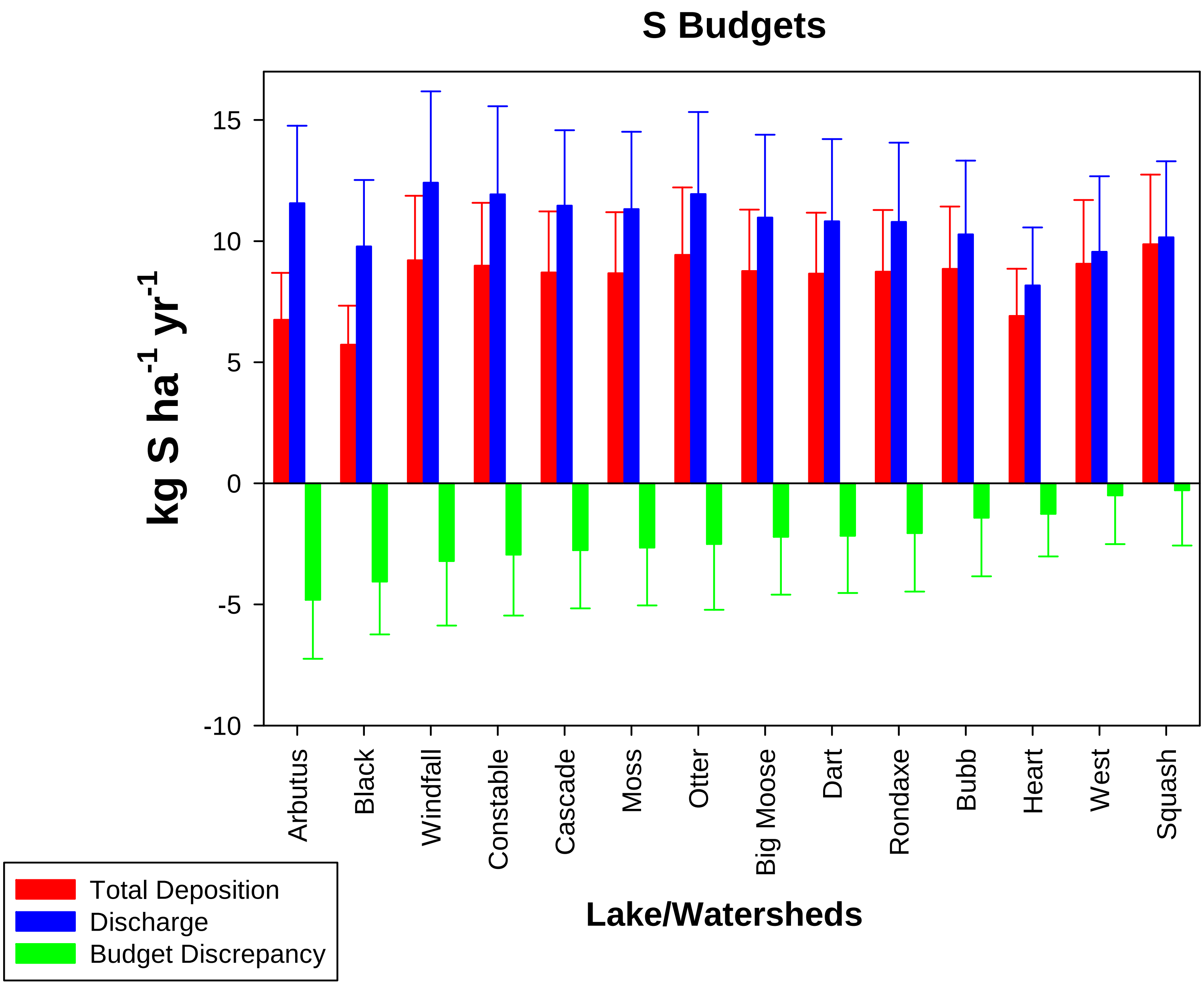

S Budgets
kg S ha-1 yr-1
15
10
5
0
-5
-10
Arbutus
Black
Windfall
Constable
Cascade
Moss
Otter
Big Moose
Dart
Rondaxe
Bubb
Heart
West
Squash
Lake/Watersheds
Total Deposition
Discharge
Budget Discrepancy

Figure 5.

Arbutus

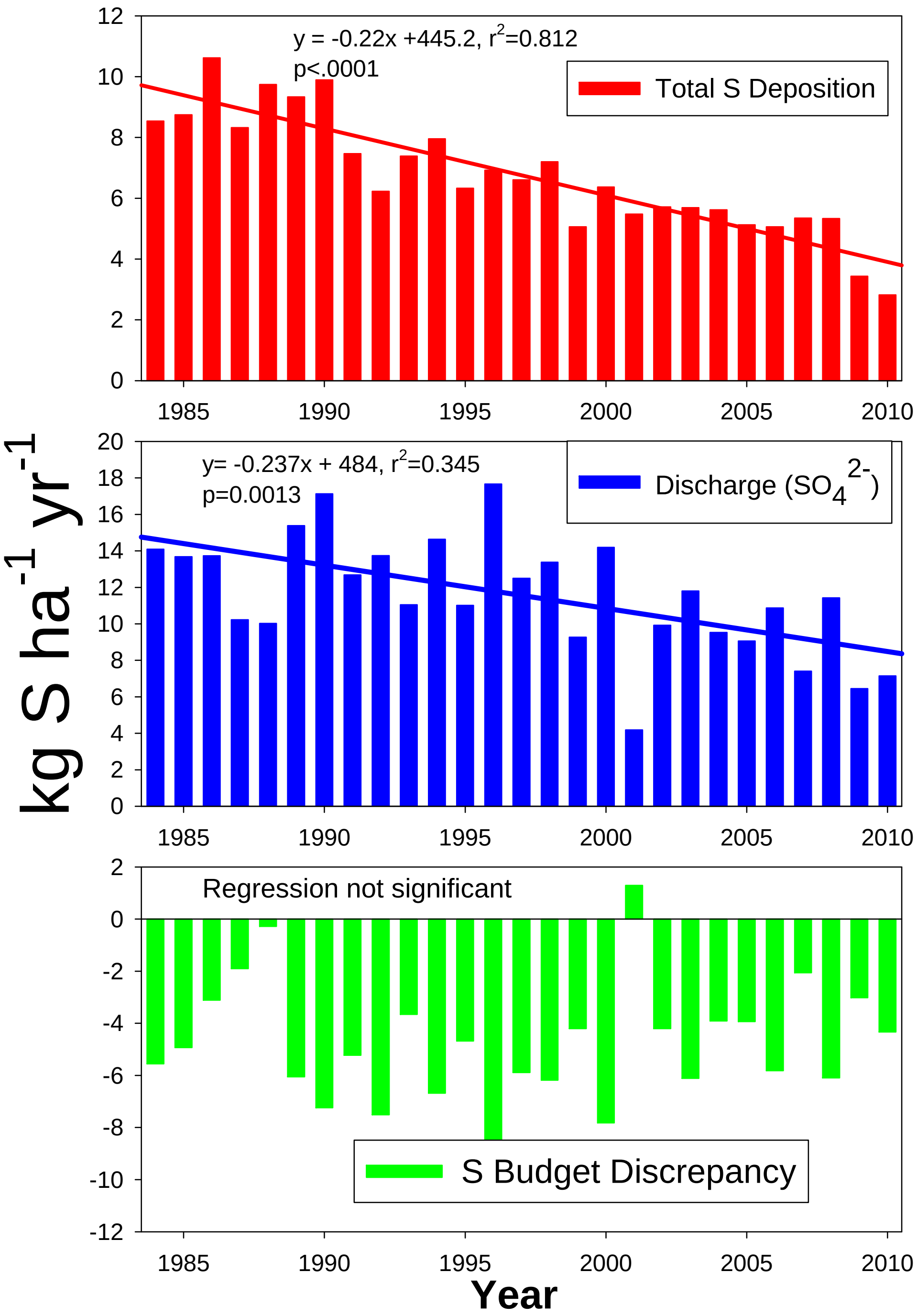


Figure 6.
Big Moose

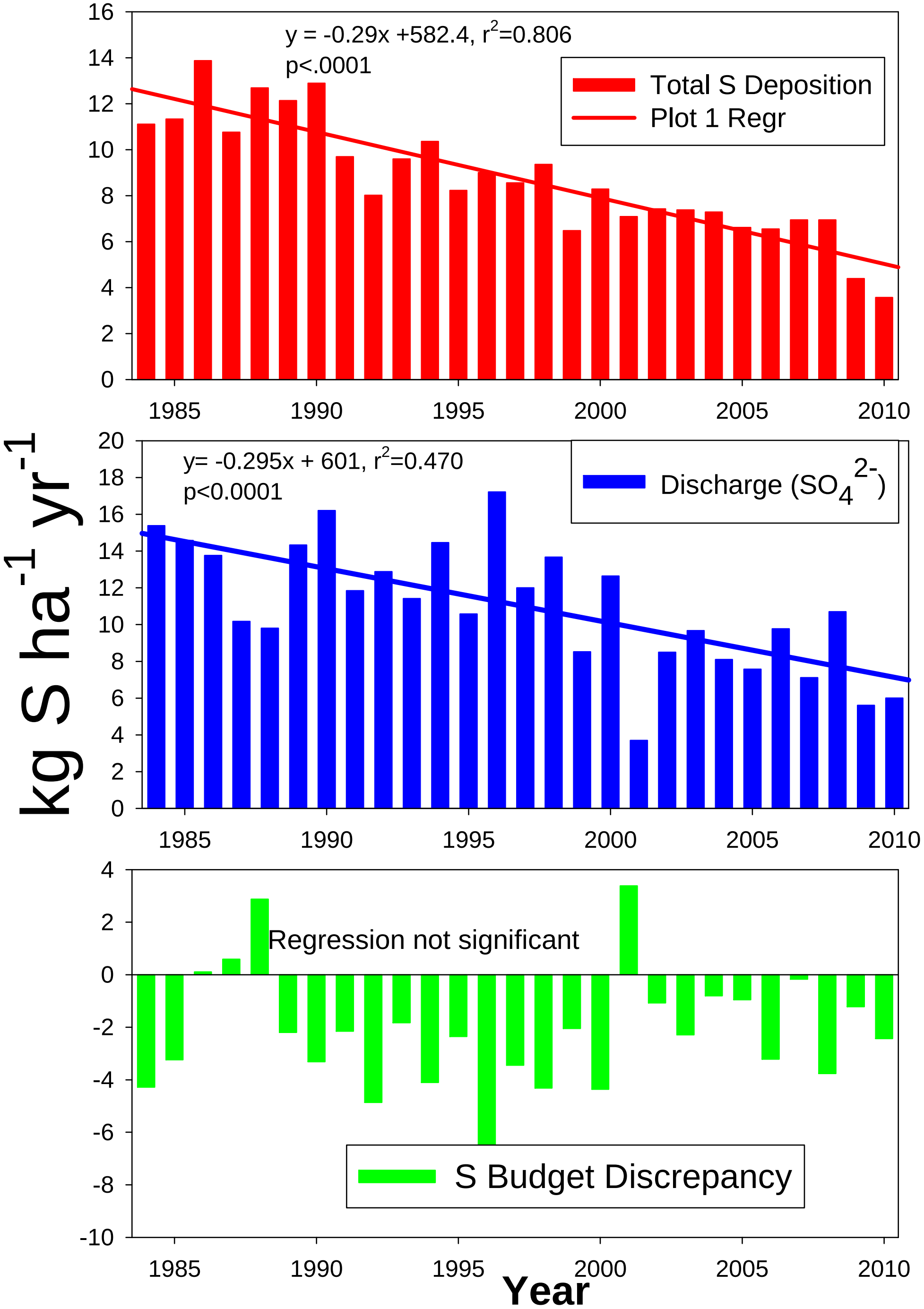
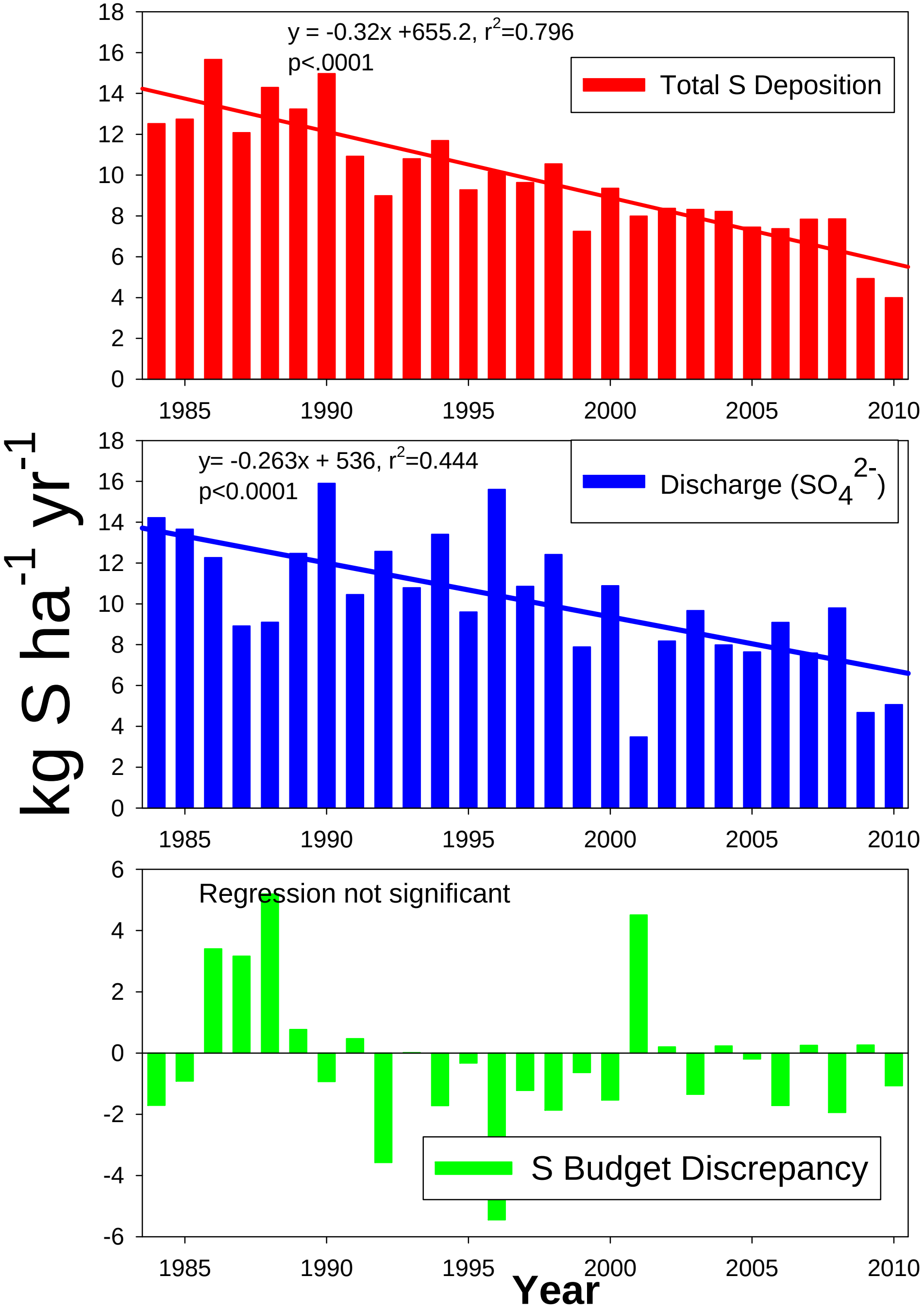


Figure 7.
Squash



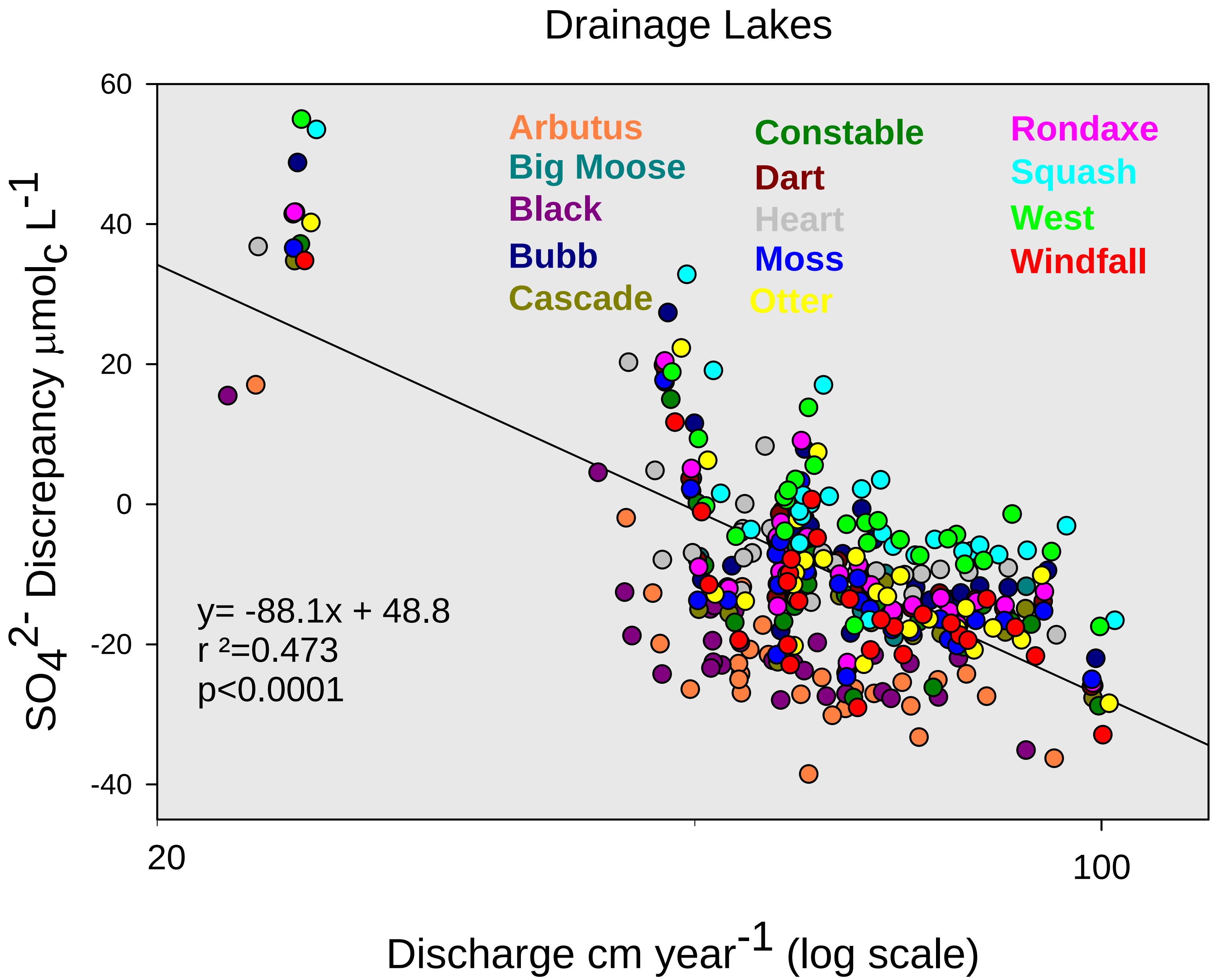
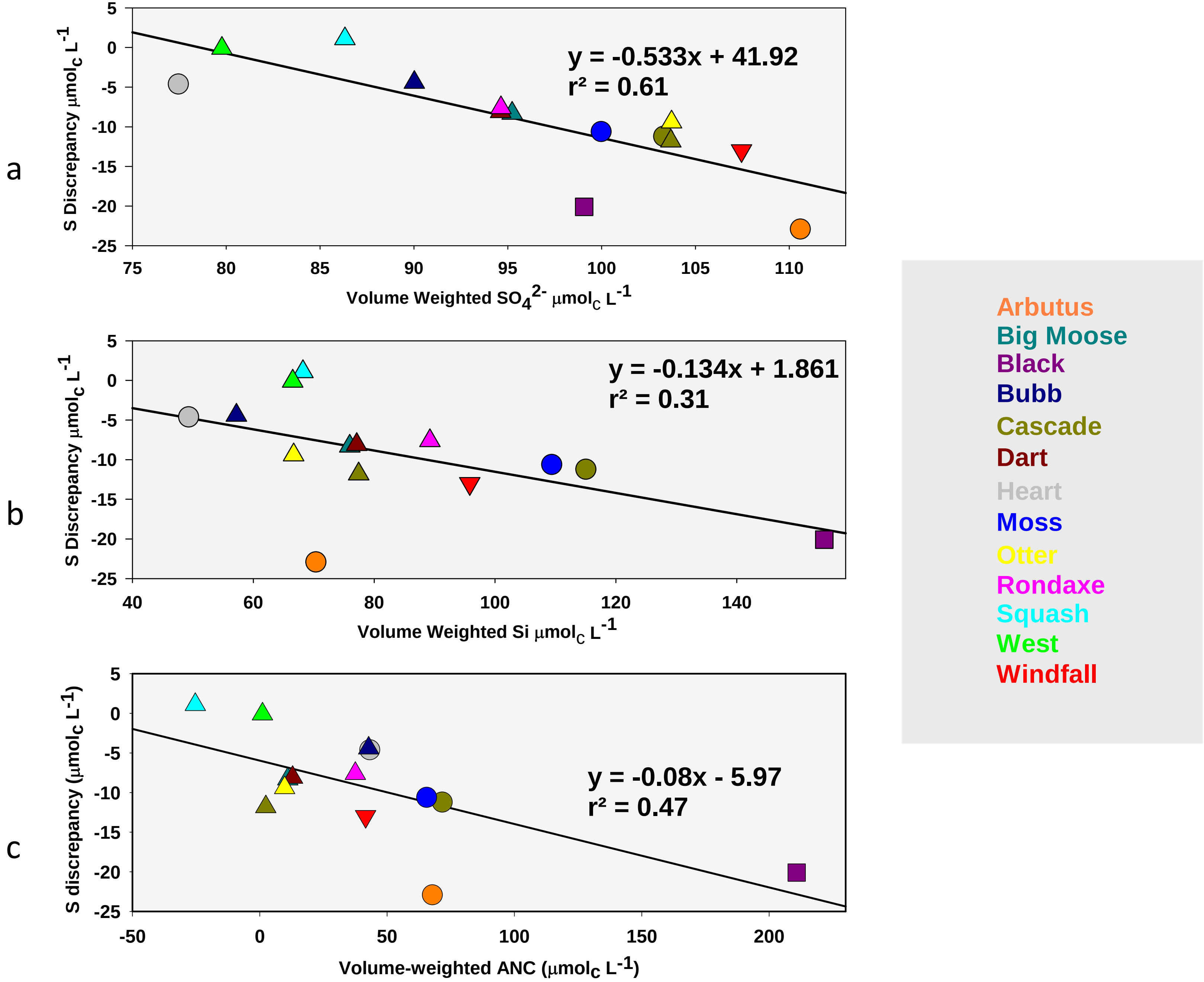

Drainage Lakes
Arbutus
Big Moose
Black
Bubb
Cascade
Constable
Dart
Heart
Moss
Otter
Rondaxe
Squash
West
Windfall
y= -88.1x + 48.8
r ²=0.473
p<0.0001
60
40
20
0
-20
-40
20
100
SO_4^{2-} Discrepancy µmol$_C$ L^{-1}
Discharge cm year^{-1} (log scale)

Figure 8

Figure 9



a
S Discrepancy µmol_c L^-1
5
0
-5
-10
-15
-20
-25
75
80
85
90
95
100
105
110
Volume Weighted SO4^2- µmol_c L^-1
y = -0.533x + 41.92
r² = 0.61
b
S Discrepancy µmol_c L^-1
40
60
80
100
120
140
Volume Weighted Si µmol_c L^-1
y = -0.134x + 1.861
r² = 0.31
c
S discrepancy (µmol_c L^-1)
-50
0
50
100
150
200
Volume-weighted ANC (µmol_c L^-1)
y = -0.08x - 5.97
r² = 0.47
Arbutus
Big Moose
Black
Bubb
Cascade
Dart
Heart
Moss
Otter
Rondaxe
Squash
West
Windfall