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**Comparisons of Watershed Sulfur Budgets in Southeast Canada and Northeast US:
New Approaches and Implications**

by

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ABSTRACT

Most of eastern North America receives elevated levels of atmospheric deposition of sulfur (S) that result from anthropogenic SO₂ emissions from fossil fuel combustion. Atmospheric S deposition has acidified sensitive terrestrial and aquatic ecosystems in this region; however, deposition has been declining since the 1970s, resulting in some recovery in previously acidified aquatic ecosystems. Accurate watershed S mass balances help to evaluate the extent to which atmospheric S deposition is retained within ecosystems, and whether internal cycling sources and biogeochemical processes may be affecting the rate of recovery from decreasing S atmospheric loads. This study evaluated S mass balances for 15 sites with watersheds in southeastern Canada and northeastern US for the period 1985 to 2002.. These 15 sites included nine in Canada (Turkey Lakes, ON; Harp Lake, ON; Plastic Lake, ON; Hermine, QC, Lake Laflamme, QC; Lake Clair, QC; Lake Tirassee, QC; Mersey, NS; Moosepit, NS) and six in the US (Arbutus Lake, NY; Biscuit Brook, NY; Sleepers River, VT; Hubbard Brook Experimental Forest, NH; Cone Pond, NH; Bear Brook Watershed, ME). Annual S wet deposition inputs were derived from measured bulk or wet-only deposition and stream export was obtained by combining drainage water fluxes with SO₄²⁻ concentrations. Dry deposition has the greatest uncertainty of any of the mass flux calculations necessary to develop accurate watershed balances, and here we developed a new method to calculate this quantity. We utilized historical information from both the US National Emissions Inventory and both the US (CASTNET) and the Canadian (CAPMoN) dry deposition networks to develop a formulation that predicted SO₂ concentrations as a function of SO₂ emissions, latitude and longitude. The SO₂ concentrations were used to predict dry deposition using relationships between concentrations and deposition flux derived from the CASTNET or CAPMoN networks. For the year 2002, we compared the

SO₂ concentrations and deposition predictions with the predictions of two continental-scale air quality models, the Community Multiscale Air Quality (CMAQ) model and A Unified Regional Air-quality Modeling System (AURAMS) that utilize complete inventories of emissions and chemical budgets. The results of this comparison indicated that the predictive relationship provides an accurate representation of SO₂ concentrations and S deposition for the region that are generally consistent with these models, and thus provides confidence that our approach could be used to develop accurate watershed S budgets for these 15 sites. Most watersheds showed large net losses of SO₄²⁻ on an annual basis, and the watershed mass balances were grouped into five categories based on the relative value of mean annual net losses or net gains. The net annual fluxes of SO₄²⁻ showed a strong relationship with hydrology; the largest net annual negative fluxes were associated with years of greatest precipitation amount and highest discharge. The important role of catchment hydrology on S budgets suggests implications for future predicted climate change as it affects patterns of precipitation and drought. The sensitivity of S budgets is likely to be greatest in watersheds with the greatest wetland area, which are particularly sensitive to drying and wetting cycles. A small number of the watersheds in this analysis were shown to have substantial S sources from mineral weathering, but most showed evidence of an internal source of SO₄²⁻, which is likely from the mineralization of organic S stored from decades of increased S deposition. Mobilization of this internal S appears to contribute about 1 to 6 kg S ha⁻¹ yr⁻¹ to stream fluxes at these sites and is affecting the rate and extent of recovery from acidification as S deposition rates have declined in recent years. This internal S source should be considered when developing critical deposition loads that will promote ecosystem recovery from acidification and the depletion of nutrient cations in the northeastern US and southeastern Canada.

INTRODUCTION

Anthropogenic emissions of sulfur dioxide (SO₂) in North America have shown marked temporal changes over the past 100 years with a maximum occurring in the early 1970s followed by a substantial decline (Figure 1). Much of this decline in the US was driven by the enactment of the Clean Air Act (CAA) in 1970 and subsequent Title IV Amendment of the CAA in 1990 as well as other regulatory controls on SO₂ emissions. Similarly, implementation of the Eastern Canada Acid Rain Program reduced Canadian emissions such that total Canada-US SO₂ emissions were 14 million tonnes in 2006 - a 50% reduction relative to 1980 levels (Canada-US, 1992, 2008). These historical emission trends are matched by changes in the atmospheric concentration and deposition of S (Lynch et al., 1996; Sickles and Shadwick, 2007; Weathers et al., 2006a). Spatially extensive and quantitatively constrained results showing these changes have been documented for wet deposition, but decreases have also been noted for components of dry deposition (composed mostly of SO₂ and SO₄²⁻ aerosols; Baumgardner et al., 2002). These decreases in atmospheric S inputs have also resulted in decreases in SO₄²⁻ concentrations in surface waters with notable decreases across southeastern Canada (Clair et al., 1995; Jeffries et al., 2003ab; Houle et al., 2004) and the northeastern US (Stoddard et al., 1999, 2003; Likens et al., 2002, 2005; Martin et al., 2000; Driscoll et al., 2003).

Elevated S deposition has been closely linked with the acidification of soils and surface waters (Reuss and Johnson, 1986; Likens et al., 1996; Weathers and Lovett, 1998). This acidification has resulted in the mobilization of toxic cations (e.g., aluminum) (Driscoll and Postek, 1996) and

the depletion of soil nutrient cations (e.g., Ca^{2+} , Mg^{2+}) (Likens et al., 1996; Fernandez et al., 2003; Bailey et al., 2005; Sullivan et al., 2006). Changes in SO_4^{2-} concentrations have been linked to effects of microbial dissimilatory sulfate reduction, an increase in methane production (Gauci et al., 2008), and the methylation of mercury (Gilmour et al., 1992). Increased concentrations of atmospheric methane are important due to the high heat trapping capacity of this “greenhouse gas” (IPCC, 2001). Methylmercury is bioaccumulated along food chains, and this chemical form of mercury is highly toxic to biota, including humans (e.g., Dennis et al., 2005).

Sulfur Pools and Budgets

Previous studies documented and summarized sulfur (S) budgets in forested ecosystems and their respective watersheds in Europe and North America. European studies have emphasized the dramatic changes in S budgets associated with those regions that had been subjected to large reductions in S deposition (Prechtel et al., 2001; Fowler et al., 2007). Studies in southeastern Canada and the northeastern US have documented that SO_4^{2-} concentrations in surface waters have also been decreasing in response to declining atmospheric deposition, but the surface water responses are often complicated by internal sources and sinks of S within ecosystems (Johnson and Mitchell, 1998; Mitchell and Alewell, 2007). The most important potential internal S sources are weathering of S minerals, mineralization of organic S, and desorption of adsorbed SO_4^{2-} (Figure 2). These internal sources can contribute to SO_4^{2-} leaching to surface waters and may delay their recovery from acidification. The importance of such responses was emphasized in a series of studies (Church et al., 1989, 1992; Cosby et al., 1991) that demonstrated the importance of SO_4^{2-} adsorption/desorption characteristics of soils. Such results have been

included in more extensive analyses of the factors affecting the SO_4^{2-} adsorption characteristics of soils (Harrison et al., 1989; Courchesne, 1992) and how they influence both long-term (e.g., Rochelle et al., 1987) and short-term (e.g., Nodvin et al., 1986; Huntington et al., 1994; Houle and Carignan, 1995) soil SO_4^{2-} dynamics and fluxes in surface waters.

There has been considerable effort placed in the evaluation of S watershed budgets in North America including comparisons among S pools and S fluxes (e.g., Johnson and Mitchell, 1998; Mitchell et al., 1992; Jeffries et al., 2003ab; Watmough et al., 2005; Mitchell and Alewell, 2007). These syntheses have found that there is a wide range of atmospheric deposition of S among sites that is a direct function of spatial patterns of SO_2 emissions. Also, the long-term temporal patterns of S deposition have been clearly linked to historical changes in SO_2 emissions (Driscoll et al., 1998, 2001; Lynch et al., 2000; Butler et al., 2001; Likens et al., 2001, 2002). Sulfate losses in drainage waters exceed estimated atmospheric inputs for most studies that have calculated watershed S budgets in southeastern Canada (Houle and Carignan 1995; Houle et al., 1997; Beall et al., 2001; Eimers and Dillon, 2002; Eimers and Houle 2005; Duchesne and Houle, 2006) and the northeastern US (Likens and Bormann, 1995; Driscoll et al., 1998; Likens et al., 2002; Park et al., 2003). The application of biogeochemical models for estimating watershed S dynamics have also suggested discrepancies as estimated by the difference between estimated atmospheric S inputs and drainage losses as SO_4^{2-} (Chen et al., 2004; Gbondo-Tugbawa et al., 2002). The role of discrepancies in ecosystem S budgets needs to be understood when making policy decisions relating the expected effect of changing emissions and resultant atmospheric deposition to ecosystem response including the response of surface waters (e.g., Driscoll et al., 2001; Sullivan and Cosby, 2005). The contribution of substantial internal S sources can affect

the establishment of critical and target loads for S deposition (Nilsson and Grennfelt, 1988). A substantial internal S source may require setting target loads at a lower level compared to sites with little or no internal S contribution to surface waters. The application of critical loads has been extensively used in Europe (Hall et al., 2001) and is currently being applied throughout Canada and the U.S. (Dupont et al., 2005; Jeffries and Ouimet, 2005; Porter et al., 2005; Ouimet et al., 2006; Burns et al., 2008; EPA, 2009).

There are, however, substantial difficulties in calculating accurate S mass balances for watersheds. Relatively accurate estimates can be made for “wet only” (or bulk) atmospheric S inputs and drainage water losses (Likens and Bormann, 1995; Mitchell et al., 2001b; Likens et al., 2002) although there can be considerable variability of wet and total deposition across landscapes (Ito et al., 2002; Weathers et al., 2000, 2006b). Comparisons of wet only and bulk S deposition estimates have generally found these measurements to be very similar in most studies (Shepard et al., 1989; Martin et al., 2000; Likens et al., 2002) although others have found some differences (Richter and Lindberg, 1988; Staelens et al., 2005). Gaseous S emissions from plants and soil are not likely to play a substantial role in temperate forest S budgets although they may be potentially more important in tropical forests (Eaton et al., 1978; Haines et al., 1989; Mitchell et al., 1992). There are major issues, however, regarding estimates of atmospheric S dry deposition, soil SO_4^{2-} adsorption/desorption, S mineral weathering and organic S immobilization/mineralization in watershed S cycling studies (Houle and Carignan, 1992; 1995; Houle et al., 2001; Johnson and Mitchell, 1998; Mitchell et al., 1992, 2001a; Likens et al., 2002; Eimers et al., 2004a).

Dry deposition is a chemical and site specific process that depends on the characteristics of the receiving surface and the local meteorology (Weathers et al., 2006b). For studying national trends in deposition, the US operates the Clean Air Status and Trends Network (CASTNET; <http://www.epa.gov/castnet/index.html>) and Canada operates the Canadian Air and Precipitation Monitoring Network (CAPMoN; http://www.msc.ec.gc.ca/capmon/index_e.cfm). These networks use an inferential approach (Hicks et al., 1987, 1991) where atmospheric concentrations are measured and multiplied by a modeled deposition velocity to obtain the deposition flux. Each network uses a different deposition velocity model with CASTNET using the Multilayer Model (Meyers et al., 1998) and CAPMoN using the Routine Deposition Model (Brook et al., 1990; Zhang et al., 2009). Spatial interpolation of the values at the network sites is difficult as there is a need to account for the changes in the underlying surface (Clarke et al., 1997; Weathers et al., 2006b). Regional air quality models such as A Unified Regional Air-quality Modeling System (AURAMS) (Smyth et al., 2007, 2008) and the Community Multiscale Air Quality model (CMAQ, Byun and Schere, 2006) provide the spatial estimates of deposition, but there are limited data from multi-year studies from these regional models. Direct deposition of cloud droplets to vegetation surfaces (cloud water deposition) can also contribute substantially to atmospheric S inputs at some sites, especially those at high elevations (Lovett et al., 1982; Lovett, 1984; Weathers et al., 1995, 2000, 2006b; Baumgardner et al., 2003; Sickles and Grimm, 2003). However, because of a lack of data and the limited area affected by the watersheds used in our study, we will not address this component of deposition in our paper.

Sulfate adsorption characteristics influence S budgets by regulating the adsorption and desorption of sulfate in soils. At the Hubbard Brook Experimental Forest in New Hampshire,

temporal patterns in solute SO_4^{2-} concentrations following tree harvesting have been attributed to changes in SO_4^{2-} adsorption characteristics caused by nitrification induced acidification (Nodvin et al., 1986; Mitchell et al., 1989). The highest SO_4^{2-} adsorption potential is found in highly weathered soils with substantial concentrations of Fe and Al sesquioxides (Reuss and Johnson, 1986; Johnson and Mitchell, 1998). Highly weathered soils in eastern North America are predominantly found south of the limit of Pleistocene glaciation, where soil forming processes have been active for hundreds of thousands of years, versus the 10,000 - 15,000 year-old soils of our study sites that were affected by more recent Wisconsinian glaciations (Rochelle et al., 1987). Within our study area, the contribution of soil SO_4^{2-} adsorption/desorption in affecting SO_4^{2-} loss or retention over multiple years is relatively small because the size of the adsorbed sulphate pool is small compared to soils in unglaciated regions (Rochelle et al., 1987; Houle and Carignan, 1995; Driscoll et al., 1998).

The precipitation and dissolution of SO_4^{2-} minerals do not generally dominate inorganic SO_4^{2-} dynamics (e.g., Johnson et al., 1982; Courchesne and Hendershot, 1990; Faseth et al., 1991; Alewell et al., 1996; Lükewille et al., 1996) except for some sites in Europe with extremely high soil solution SO_4^{2-} and aluminum concentrations that may result in jurbanite formation (Nordstrom, 1982; Khana et al., 1987). For many well-studied watersheds the results suggest that the weathering of S minerals is not the major source of S (Likens et al., 2002; Mitchell and Alewell, 2007). However, in some watersheds there may be substantial amounts of S minerals in some geological formations (e.g., shales, sulfidic micaceous phyllites) that may constitute an important internal source of S (Mitchell et al., 1986; Shanley et al., 2005). The contribution of

the weathering of S minerals can affect the SO_4^{2-} isotopic composition of drainage waters in those watersheds where S minerals are important (Bailey et al., 2004).

For temperate forests generally more than 84% of S occurs within the mineral soil and generally more than 80% of this S is organic (e.g., carbon-bonded S, ester sulfates) (Houle and Carigan, 1992; Mitchell et al., 1992). The contribution of organic S dynamics to watershed budgets has been the focus of considerable attention due to its large pool size of which small changes could have dramatic effects on S export in drainage waters. Evidence using natural SO_4^{2-} isotope abundances (both $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) from studies of forest ecosystems both in North America (Gélineau et al., 1989; Zhang et al., 1998; Alewell et al., 1999; Eimers et al., 2004c; Eimers and Houle, 2005; Schiff et al., 2005) and Europe (Alewell and Gehre 1999; Mayer et al., 1995; Novák et al., 2005, 2007) has indicated the importance of the immobilization of SO_4^{2-} and organic S mineralization in affecting ecosystem S dynamics.

NEW APPROACHES FOR ASSESSING WATERSHED SULFUR BUDGETS

Given the decreases in S emissions and deposition that have been measured in eastern North America since the 1970s (Figure 1), there is an important need to examine how these changes have affected the S export from watersheds throughout the region. Our overarching objective was to evaluate and compare S budgets in well-studied watersheds in the northeastern US and southeastern Canada. We were also able to compare changes in S budgets over the period of our study. In Table 1 we give information for each site including: the watershed's name, location, size, soil type, dominant vegetation, and key references. The locations of the watersheds are

shown in Figure 3. We have developed a series of calculations that use a consistent approach to provide common metrics for comparing similarities and differences among the watershed S budgets. Watersheds were selected based upon the availability of information on S precipitation inputs and drainage water SO_4^{2-} losses over an extended period. Some of the watersheds have had additional studies on S pools and fluxes including the utilization of isotopic analyses. We have based our mass budget analyses on the well-established procedures and assumptions that have been used extensively for small watersheds (Likens and Bormann, 1995; Moldan and Cerny, 1995). As is typical for watershed studies that have well-documented hydrology and chemistry, we have substantial confidence in the estimates of S precipitation inputs and S drainage losses.

We hypothesized that most of the watersheds in our 15 study sites would show S outputs that exceed inputs due to losses through some combination of S mineral weathering, losses from soil organic matter, and desorption from the mineral soil. This hypothesis is supported by numerous studies that have found net S losses in drainage water in forested watersheds of southeast Canada and the northeast US. Our study approach recognized the difficulty and uncertainty of quantifying dry deposition inputs of S (e.g., Lovett, 1994; Weathers et al., 2000, 2006b). Here, we applied two approaches to the entire study period for estimating dry S inputs using empirical equations using dry deposition estimates from (1) CASTNET and (2) CAPMoN. We also made comparisons using the regional CMAQ and AURAMS model for year 2002 (the year for which model results were available during our study period). All statistical analyses were performed using SAS for Windows ®Version 9.1.3 (SAS Institute Inc., Cary, NC, USA).

Precipitation and Drainage Water

This synthesis is based on calendar-year budgets of atmospheric inputs and drainage water exports. The period of record and basic information on the frequency of collection and any differences among sites in measurement approaches (e.g., bulk deposition versus wet-only deposition) are provided in Table 2. Annual values for precipitation and drainage amounts were based upon the summation of measurements during each year for each site. Concentrations for precipitation and stream export were volume weighted (e.g., by precipitation amount or discharge rate) for each collection period, converted to fluxes using precipitation and drainage water values and summed for each calendar-year. For most watersheds, precipitation amounts were measured daily and concentration measurements were based upon weekly collections. Discharge measurements were made at different intervals (ranging from continuous to mean average daily values) and chemistry measurements were generally made on a weekly basis with any exceptions noted. For Turkey Lakes the discharge and stream export data used here were an average of 13 watersheds (watersheds 31-35, 37-39, 42, 46-47, 49-50). We selected the 17-year period from 1985 to 2002 as the period for comparison because of data completeness. For some watersheds only a portion of this period was available. Also, for a few watersheds longer records were available beyond our selected study period. We compared S budgets among these watersheds using different periods and did not find any marked differences in overall budget patterns.

Dry Deposition

Obtaining accurate and consistent long-term estimates of dry deposition for use in mass balance studies is a major challenge. Many of the watersheds used in this comparison did not have dry deposition estimates available on site; therefore, we required an approach for estimating annual dry deposition for all sites that **1) provided estimates for each site, 2) was consistent in methodology across sites, and 3) was able to make annual estimates over time as S emissions changed**. To meet these criteria, we developed a two-step approach. In the first step, we used SO₂ concentration data from dry deposition monitoring networks in the northeastern US (CASTNET) and southeastern Canada (CAPMoN) along with annual Eastern US SO₂ emissions data to develop an empirical relationship. This relationship was then used to determine the spatial and temporal patterns of SO₂ concentrations in the air at the watershed locations. To match the geographical area of the watersheds we were studying, we used SO₂ concentration data only from sites > 40°N latitude and <85°W longitude from both the CASTNET (US) and CAPMoN (Canada) dry deposition monitoring networks. There were 23 sites included in this geographical area, 16 in the US and seven in Canada (Figure 3). The estimates of annual SO₂ emissions were derived from the US EPA estimates of the Acid Rain Program sources located in Eastern US (EPA Regions 1 through 5):

<http://camddataandmaps.epa.gov/gdm/index.cfm?fuseaction=emissions.wizard>. Previous analyses have indicated that the Canadian SO₂ emissions constitute a small (~10%) proportion of the total and hence would not markedly affect this relationship (for further information see: Canada-United States Air Quality Agreement: 2008 Progress Report; Vet and Ro, 2008). The yearly estimated eastern US SO₂ emissions declined substantially for the period of our study (1985-2002) (Figure 1), illustrating the importance of including a temporal component to the dry

deposition calculations. Note that SO₂ emissions data were available from the US EPA only for the years 1985, 1990, 1995, and then annually thereafter, so for the periods 1986-1989 and 1991-1994, we linearly interpolated emissions data based on emissions before and after the period for 1987, 1988, 1992 and 1993 for calculations for those years.

A variety of possible relationships between annual average atmospheric SO₂ concentration and latitude, longitude and annual eastern US SO₂ emissions were tested and we found that an asymptotic exponential function (Equation 1, Figure 4) explained 88% of the variation in predicted versus observed SO₂ concentrations with little bias (slope of 1.0).

Equation 1)

$$SO_{2ave} = 0.9 + \exp(7.867 - 0.4633*lat + 0.1494*long + 1.863e-7*toteastSO_2)$$

where SO_{2ave} is the annual average SO₂ concentration (µg m⁻³) for each site and year, lat is ° north latitude, long is ° west longitude, and toteastSO₂ is the total emissions (tons per year) of SO₂ from the eastern US for the year.

Using Equation 1, the average annual SO₂ concentrations for each site were calculated. The mean and range of SO₂ concentrations across the years of the study are shown in Figure 5 with sites ranked by latitude from south to north. For all sites the mean SO₂ concentration was 1.2 µg S-SO₂ m⁻³, the maximum concentration was at Biscuit Brook (3.2 µg S-SO₂ m⁻³) and the minimum concentration at Lake Tirasse (0.5 µg S-SO₂ m⁻³) (Figure 5). To examine the potential impact of local sources and the effects of not including chemical transformations, we compared

output for the year 2002 (the only year where complete data were available) from the regional air quality models CMAQ (Byun and Schere, 2006) and AURAMS (Smyth et al., 2007), which were run using the full US and Canada emissions inventories, with the values predicted for each watershed from Equation 1. Details on specific CMAQ and AURAMS applications can be found in Appel and Roselle (2009) and Moran et al. (2008), respectively. Together the results from the CMAQ and AURAMS models give a sense of the results expected from a spatially explicit treatment of emissions, transport, and transformation compared with the simplified empirical approach used in our study. There is a notable difference between the CMAQ and AURAMS estimates for the Lake Clair watershed where a local SO₂ source (Alcoa aluminum smelter) was located within the AURAMS grid cell (Moran, unpublished data), but not within the CMAQ grid cell. Figure 6 shows that concentrations estimated using Equation 1 are quite similar to those predicted by the two regional air quality models for most sites. If we exclude the Lake Clair SO₂ estimate for AURAMS, there are strong and highly significant correlations ($r = 0.731$ to 0.886 , $p < 0.01$) among SO₂ concentration estimates for each site using Equation 1, AURAMS and CMAQ.

In the second step, we used data from all 86 CASTNET sites for years 1990-2003 and from the 11 CAPMoN sites for years 1998-2002 (the number of years with results varied among sites) to derive an empirical relationship between annual average SO₂ concentration and modeled total S dry deposition (SO₂ plus SO₄ particles) using the CASTNET and CAPMoN data sets separately. We also evaluated the CASTNET relationship using a subset of sites (e.g., forested sites in the northeast US) and found no substantial difference in this empirical relationship using this more limited data set. Previous studies comparing concentration values from CASTNET and

CAPMoN at a co-located site in Egbert, showed that the measured air concentrations for SO₂ and SO₄²⁻ were almost identical for the CASTNET and CAPMoN measurements, but the CAPMoN deposition estimates for SO₂ and SO₄²⁻ were substantially greater due to different models of deposition velocity (Vet et al., 2005). As a result of the differences in the deposition models, the data from each network give different relationships between SO₂ concentration and total S dry deposition (Figure 7). The two equations are:

Equation 2)

CASTNET Equation:

$$\text{kg S ha}^{-1} \text{ yr}^{-1} = \text{SO}_2 (\mu\text{g S m}^{-3}) * 1.169 + 0.00572$$

$$r^2 = 0.901$$

where SO₂ values are average yearly concentrations for each CASTNET site.

Equation 3)

CAPMoN equation:

$$\text{kg S ha}^{-1} \text{ yr}^{-1} = \text{SO}_2 (\mu\text{g S m}^{-3}) * 1.696 + 0.694$$

$$r^2 = 0.928$$

where SO₂ values are average yearly concentrations for each CAPMoN site.

Equations 2 and 3 demonstrate the uncertainty associated with models of deposition velocity. Use of other deposition formulations such as those used in CMAQ and AURAMS will result in different estimates of the deposition velocity. The various deposition models used in CASTNET, CAPMoN, CMAQ and AURAMS produce estimates of deposition velocity that are comparable to field estimates (e.g., Meyers et al., 1998; Finkelstein et al., 2000; Pleim et al. 2001; Zhang et al., 2001), but are not in agreement with each other. Comparing the estimates

from equations 2 and 3 with the deposition estimates from CMAQ and AURAMS provides a more complete depiction of the uncertainty associated with the deposition velocity estimates at the watershed sites than just Equations 2 and 3 alone (Figure 8). As noted previously there is a notable difference for the Lake Clair watershed where a local SO₂ source is located within the AURAMS grid cell (Moran, unpublished data), but not within the CMAQ grid cell, and not sufficiently close to the network monitoring sites to influence the regression equation. There was a strong and significant correlation ($r=0.607$ to 0.880 , $p\leq 0.02$) between the dry S deposition estimates among sites for year 2002 using AURAMS, CMAQ, Equation 2 and Equation 3 excluding Lake Clair. Because data are needed for the complete period of the study, for the remainder of our current analyses we have used Equations 2 and 3 to estimate dry deposition at each watershed location and to provide a sense of how the uncertainty in the dry deposition estimates affects S mass balance budgets.

WATERSHED BUDGETS

Water Budgets

The mean annual precipitation for all the watersheds for the period from 1985 to 2002 was 1215 mm with minimum annual precipitation (800 mm) occurring at Lake Tirassee and the maximum (1800 mm) at Biscuit Brook (Figure 9). The average annual discharge amount for this same period for all watersheds was 737 mm with minimum (441 mm) at Hermine and a maximum (969 mm) at Moosepit. Average annual calculated evapotranspiration (precipitation - discharge) for this same period for all watersheds was 478 mm with minimum (223 mm) at Lake Tirassee

and a maximum (721 mm) at Hermine. The mean annual precipitation, discharge and evapotranspiration values for each watershed are provided in Figure 9.

Sulfur Budgets Including Estimates of Dry Deposition using Formulations Based upon Measurements from CASTNET and CAPMoN

The use of the CASTNET-based Equation 2 estimates for total dry S deposition resulted in a mean dry deposition of $1.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ with a minimum at Lake Tirasse ($0.6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) and a maximum at Biscuit Brook ($3.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$). The use of CAPMoN-based Equation 3 resulted in substantially higher mean dry deposition estimates of $2.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ with a minimum at Lake Tirasse ($1.6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) and a maximum at Biscuit Brook ($6.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$). Average SO_4^{2-} discharge among watersheds was $11.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ with a large range among watersheds from $4.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ (Lake Tirasse) to $17.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ (Sleepers River) (Figure 10). The inclusion of the estimates of S dry deposition combined with S precipitation inputs were used to calculate average differences in total atmospheric inputs versus losses from discharge for each of the watersheds (Figure 10). The use of Equation 2 resulted in a mean discrepancy of $-3.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ with the smallest ($+0.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) at Hermine, which was the only watershed to show net S retention using this estimate of total atmospheric deposition, and a largest ($-10.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) at Sleepers River. Using this latter estimate, four watersheds out of the 15 sites showed net S retention (Hermine: $+1.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Lake Tirasse: $+0.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Turkey Lakes: $+0.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Moosepit: $+0.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$). The use of Equation 3 resulted in a lower mean discrepancy of $-2.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ with the smallest difference (-0.2 and $+0.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) at (Mersey and Moosepit, respectively) and largest difference ($-10.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) at Sleepers River.

INDIVIDUAL WATERSHED SULFUR BUDGET RESULTS AND COMPARISONS AMONG WATERSHEDS

Temporal Patterns

For the study period from 1985 through 2002, regression analyses ($p \leq 0.05$) were used to evaluate temporal changes in various components of the S budget of each site. In addition to the flux measurements, we also estimated annual, volume-weighted sulfate concentrations of precipitation and stream discharge in $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$. Using appropriate conversions from mass to molar values and dividing the annual SO_4^{2-} flux value of precipitation or discharge ($\text{kg S-SO}_4^{2-} \text{ ha}^{-1} \text{ yr}^{-1}$) by water flux (mm yr^{-1}), we converted these values to $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$. Using linear regression, we found that the three measured attributes that showed the most consistent and significant relationships over time were S precipitation flux and SO_4^{2-} concentration in precipitation and drainage water (Table 3). For the 15 watershed locations two pairs of sites used the same S precipitation inputs (Plastic Lake and Harp Lake; Mersey and Moosepit) and each pair showed significant decreases in S inputs. For the other 11 watershed locations, seven showed a significant reduction in precipitation S inputs over time. Similar, but fewer significant results were also found for changes in SO_4^{2-} concentration in precipitation with the two paired sites showing declines. For the other 11 locations, five sites showed significant ($p \leq 0.05$) decreases in SO_4^{2-} concentration in precipitation over time. As expected, there were also significant changes in SO_4^{2-} concentration in drainage water with eight of 15 sites showing significant declines in SO_4^{2-} concentration over time (Table 3). The lack of significant changes

over time in SO_4^{2-} concentration for some sites was likely due in part to the absence of complete coverage within the period of analyses for those sites with lowest deposition and fewest years of record (See Table 2 for more details on years covered).

An examination of the patterns of S precipitation inputs, discharge and discrepancies in annual values showed considerable variation among years. Annual SO_4^{2-} budgets are provided for Hubbard Brook Experimental Forest Watershed 6 (Figure 11) and Turkey Lakes (Figure 12) along with their respective annual hydrological fluxes (Figures 13 and 14, respectively) to illustrate the importance of this annual variation. For example, note the correspondence with high water discharge and SO_4^{2-} loss at the Hubbard Brook Experimental Forest in 1990 and 1996. At Turkey Lakes the highest discharge and SO_4^{2-} loss occurred in 1988. Similar results are apparent for all the watersheds used in our study (detailed results not shown). The importance of watershed hydrology in affecting temporal variation of SO_4^{2-} concentrations has been reported previously within the study region with particular attention to the role of drying and wetting in affecting SO_4^{2-} mobilization (Eimers and Dillon, 2002; Jeffries et al., 2003b; Eimers et al., 2007; Mitchell et al., 2008).

Comparisons of Sulfur Budget Differences among Watersheds

To facilitate the temporal and spatial comparisons of the watersheds, the discrepancies in annual S budgets in $\text{kg S ha}^{-1} \text{ yr}^{-1}$ were converted to mean annual, volume-weighted concentration values ($\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) using the annual stream discharge for each watershed. This conversion to concentrations facilitates comparisons of S budget discrepancies among watersheds and over time since the interannual S drainage water fluxes for each catchment are greatly affected by

differences in annual water discharge as discussed above. The mean annual concentration discrepancies (ranked from most negative to most positive) for each site using precipitation plus dry deposition (Equation 2: CASTNET values; Equation 3: CAPMoN values) are provided in Figure 15. Only Lake Laflamme showed a significant trend in concentration discrepancies over time (total deposition using Equation 2: slope = $0.908 \mu\text{mol SO}_4^{2-} \text{ yr}^{-1}$, $p \leq 0.0001$; total deposition using Equation 3: slope = $0.880 \mu\text{mol SO}_4^{2-} \text{ yr}^{-1}$, $p = 0.0001$) suggesting that these discrepancies have remained relatively similar over the period of study for almost all of the watersheds.

Typical results of annual variation are shown for Arbutus, Biscuit Brook and Moosepit watersheds (Figure 16). Some of the variation in these concentration discrepancies among years can be attributed to watershed precipitation and hence hydrological relationships. This relationship was evaluated by regressing the annual concentration discrepancies against annual precipitation for each site. For eight out of the fifteen sites there was a significant inverse relationship between annual precipitation and concentration discrepancies (Table 4) suggesting the importance of hydrology in the regulation of SO_4^{2-} in drainage waters. Studies at many of these sites (Plastic Lake: Eimers and Dillon, 2002; Eimers et al., 2004ac; Arbutus: Mitchell et al., 2006, 2008; Sleepers River: Mitchell et al., 2008, Shanley et al., 2008; Cone Pond: Mitchell et al., 2008; Turkey Lakes: Schiff et al., 2005) have established the importance of changing hydrology in affecting S dynamics due to the linkages among watershed wetness, redox conditions and SO_4^{2-} mobilization.

An examination of the mean SO_4^{2-} concentration discrepancies suggest that the 15 sites can be categorized based upon the range of these values (Figure 15). For more details on the S budgets and biogeochemistry of individual sites see Appendix I.

Category I: Clearly, Sleepers River has the greatest discrepancy (-37 to -42 $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) of all other sites by $>13 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$ and hence the largest internal S source of all watersheds in the current study. The source of this discrepancy has been previously identified, using mass budgets and stable isotopic analyses of S sources, to be weatherable S minerals (Bailey et al., 2004; Shanley et al., 2005), with possible occasional contributions from reoxidized secondary sulfides (Shanley et al., 2008).

Category II: These sites (Bear Brook, Harp, Arbutus, and Cone Pond) have concentration discrepancies from -20 to -27 $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$ (using Equation 2 estimates) or -14 to -23 $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$ (using Equation 3 estimates) and some have evidence of internal S sources. At Bear Brook experimental work using “mineral soil bags” has shown that much of the short-term variation and response to S additions were due to changes in adsorbed SO_4^{2-} (David et al., 1990). Previous isotopic analyses ($\delta^{34}\text{S} - \text{SO}_4^{2-}$) at Bear Brook suggested that most of the SO_4^{2-} in discharge can be attributed to S derived from atmospheric deposition, but an additional unknown internal S source was likely present (Stam et al., 1992). Harp Lake Watershed (HP3A) is predominantly upland, and as a consequence SO_4^{2-} concentrations in stream water are much less variable over time (Eimers et al., 2008; Seip et al., 1985) than nearby Plastic Lake as discussed below. Previous analysis at Arbutus watershed, including estimates of dry deposition, suggested that an internal S source was required to balance the S budget (Park et al., 2003). Results using SO_4^{2-} isotopic evidence ($\delta^{18}\text{O}$ and $\delta^{34}\text{S}$) (Campbell et al., 2006) and spatial patterns of SO_4^{2-} concentrations (Piatek et al., 2009) have suggested that some subcatchments of the Arbutus Watershed have a strong internal S source. Previous work at Cone Pond has suggested the potential importance of a fire in 1820 that heavily burned 85% of the watershed. It has been

suggested that this fire reduced the organic matter content with a resultant effect on SO_4^{2-} dynamics (Mitchell et al., 2008).

Category III: These sites (Lake Laflamme, Plastic, Lake Clair, HBEF and Biscuit Brook) have concentration discrepancies lower (i.e., less negative) than Category II. The values range from -12 to -14 $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$ (using Equation 2 estimates) or -3 to -10 $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$ (using Equation 3 estimates). For this category, although the discrepancies are smaller than those in Category II, they all show a net loss of SO_4^{2-} . Previous studies at Lake Laflamme Watershed have indicated that soil SO_4^{2-} sorption should adjust rapidly (within 4 years) to changing S loads but that desorption alone cannot explain long-term net SO_4^{2-} losses (Houle and Carignan, 1995). An oxygen isotope study of the dissolved SO_4^{2-} in soil solution demonstrated that 32-61% of the SO_4^{2-} leaving the catchment had interacted with organic S in the soil (Gélineau et al., 1989). Previous work at Plastic Lake (PC1) Watershed has indicated that sulfate export was strongly influenced by the presence of a large conifer-*Sphagnum* swamp (e.g., LaZerte 1993; Eimers and Dillon 2002; Eimers et al., 2007; Aherne et al., 2008). Stable isotopic analyses have shown that changes in SO_4^{2-} concentration at this watershed are associated with microbial redox processes (Eimers et al., 2004ab). Previous investigations at Lake Clair Watershed attributed net S losses to a combination of SO_4^{2-} desorption and/or organic S mineralization (Houle et al., 1997). At the Hubbard Brook Experimental Forest, there has been considerable effort associated with the evaluation of S budgets since 1964 (e.g., Likens and Bormann, 1995; Likens et al., 2002). This previous work has also suggested that there is a discrepancy in the net hydrologic S budgets (precipitation inputs minus streamwater outputs) for the various watersheds of the Hubbard Brook Experimental Forest including W6 used in the current study. The use of isotopic analyses ($\delta^{34}\text{S}$) of SO_4^{2-} has

suggested that the discrepancy is likely due to the mineralization of a small fraction of the large organic S pool (Alewell et al., 1999). The use of the PnET-BGC simulation model also support the importance of the mineralization of the organic S pool in the soil as the major contributor to the discrepancy in the net hydrologic S budget (Gbondo-Tugbawa et al., 2002). There is no evidence that weathering is a substantial S source (Likens et al., 2002; Bailey et al., 2004). At Biscuit Brook, the results of the current study indicate a substantial net watershed loss of S and differ from an earlier study in which S inputs were estimated to approximately balance outputs when dry S deposition was assumed to equal 33% of wet S deposition (Stoddard and Murdoch, 1991). This earlier study was only for two years and used results from a period (1984-1985) with higher rates of S deposition than for the average for the entire period (1985-2002) of the current study.

Category IV: These sites (Turkey Lakes, Mersey, Lake Tirasse and Moosepit) are characterized by concentration discrepancies near zero (-6 to $+3 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$). For all of these sites, except Mersey, the utilization of the higher dry deposition estimates using Equation 3 resulted in small net S retention. All four of the sites in Category IV are in Canada and relatively remote from major sources of anthropogenic S deposition (Figure 3). Previous studies at Turkey Lakes have ascribed some of the decrease in stream SO_4^{2-} to losses of exchangeable SO_4^{2-} from upper soils layers (Morrison et al., 1992; Beall et al., 2001 Morrison and Foster 2001). Watershed S discrepancies at Lake Tirasse Watershed of $0.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$ have been previously documented using throughfall S deposition, plus the contribution of dissolved organic sulfur (DOS) in incoming precipitation as a surrogate for total S deposition from 1997-2003. These previous studies have also suggested that mineralization of soil organic S was the likely source of the

excess S (Duchesne and Houle, 2006). For Moosepit Watershed, the results of the current study provide a different estimate from that of Yanni et al. (2000) who ascribed a discrepancy between measured wet CAPMoN S deposition and export to unmeasured fog deposition.

Category V: The Hermine site is very distinctive with exceptionally positive discrepancies ($> +14 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) suggesting strong S retention in this watershed. However, Hermine has a discharge ratio (discharge/precipitation) of about 38%, a low value for forested watersheds of Northeastern North America. Along with the Turkey Lakes and Lake Tirassee catchments (using Equation 3), Hermine is the only watershed apparently retaining S on a mean annual basis using equations 2 and 3. In all cases, these years were much dryer than average with less than 1150 mm precipitation and high summer temperatures that caused streamflow to cease for prolonged periods during the growing season. Sulfur was lost (-1.2 to $-4.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ with Equation 3) from the watershed when the Hermine experienced cooler and much wetter conditions.

CONCLUSIONS

Our analyses underscore the importance of having accurate estimates of atmospheric deposition, both wet and dry, for assessing S budgets for watersheds in southeastern Canada and the northeastern US. Although relatively accurate values for the wet deposition of S are available, the contribution of dry deposition is more difficult to quantify because of the inherent difficulties in estimating dry deposition to the landscape. An evaluation of the contribution of dry deposition is needed, however, for making both temporal and spatial analyses of S budgets and relating these budgets to changes in the emissions of SO_2 . We developed an empirical approach for estimating

dry deposition based upon results available from both the US (CASTNET) and Canadian (CAPMoN) dry deposition networks to provide a range of estimates. This empirical approach included the use of regional S emissions to the general region, SO₂ concentrations, and spatial location. We also compared these empirical results with the results from the CMAQ and AURAMS models for 2002 to help further our understanding of approaches for evaluating dry deposition. Using estimates of total S deposition we evaluated S budgets for 15 watershed sites and found substantial differences among these budgets.

For some watersheds such as Sleepers River (Category I) the importance of the weathering of S-bearing minerals resulted in a substantial source of SO₄²⁻ to drainage waters. For other relatively remote sites in Canada such as Turkey Lakes, Mersey, Lake Tirasse and Moosepit (Category IV), the results suggested that S inputs are relatively closely matched with SO₄²⁻ losses in drainage waters. For the majority of the watersheds included in our study (especially categories I to III), there was an additional source of S and our analyses suggest that this contribution is relatively constant within a site among years. A range of the contribution of this internal S source can be calculated by using a range of SO₄²⁻ discrepancy values (i.e., -3 to -27 μmol SO₄²⁻ L⁻¹; Figure 15; Categories II and III) and using the average annual discharge for the 15 sites (737 mm yr⁻¹). We excluded Sleepers River with its known mineral S sources and those watersheds (Category IV) that have not been subjected to lower levels of atmospheric deposition of S. This calculation suggests that **internal S sources can contribute an additional 1 to 6 kg S ha⁻¹ yr⁻¹ in the annual SO₄²⁻ export**. Other studies have suggested that although there may be some contribution from the desorption of SO₄²⁻ that accumulated during periods of higher S deposition, but the SO₄²⁻ adsorption capacities of the soils in this region are relatively small (Rochelle et al., 1987; Mitchell

et al., 1992; Houle and Carigan, 1995). Mass balance calculations suggest that only a relatively small proportion of the discrepancy in watershed S budgets can be attributed to SO_4^{2-} desorption (Driscoll et al., 1998). Although the source of this additional S is not known with complete certainty, stable isotopic analyses studies both in North America (Allewell et al., 1999, 2000; Likens et al., 2002; G lineau et al., 1989) and Europe (Nov k et al., 2005, 2007) have strongly suggested that the mineralization of organic S in soil could be an important source. The results of the current study suggest that this internal source is more important for those sites that have been subjected to elevated levels of atmospheric S deposition (e.g., Harp Lake, Arbutus, Plastic, HBEF, Biscuit Brook) compared to those sites that have had relatively low amounts of atmospheric S inputs (Mersey, Lake Tirasse, Moosepit). This finding is supported by a significant ($r^2 = 0.54$, $p=0.02$) positive relationship between the S budget discrepancy (including dry deposition estimates provided by Equation 2) versus S precipitation inputs during the period of the study for watersheds in Categories III and IV for which S weathering inputs are likely very small based upon their known mineralogy.

The factors that affect the mobilization of previously stored S are not completely understood although we do know that watershed hydrology can have a major influence on SO_4^{2-} drainage losses and retention. Some of these factors are associated with effects related to the mobilization of SO_4^{2-} formed from previously reduced S especially in wetlands (e.g., Schiff et al., 2005; Eimers et al., 2007; Mitchell et al., 2008). Watershed wetness also affects the connectivity of surface waters to solute sources (Creed and Band, 1998; Inamdar et al., 2004) and increased wetness would likely result in the enhanced SO_4^{2-} movement from soils to streams. Changing climate conditions and the resultant effects on the hydrology and S biogeochemistry of eastern North

American forests are likely to be important in the future (e.g., Campbell et al., 2009; Huntington et al., 2009).

The surface waters of southeastern Canada and the northeastern U.S. have shown substantial recovery from high levels of S deposition, but the contribution of these internal additional sources of S needs to be considered in evaluating the long-term recovery of terrestrial ecosystems. As atmospheric S inputs decrease, the relative importance of internal S sources in contributing to the SO_4^{2-} in drainage waters will increase. Moreover, recent evidence has suggested that soils within this region have become depleted in nutrient cations such as calcium and magnesium (Fernandez et al., 2003; Bailey et al., 2005; Sullivan et al., 2006). The atmospheric input of S and the mobilization of the SO_4^{2-} anion from internal S sources will not only exacerbate the loss of base cations but will also contribute to the continued acidification of soils and surface waters by the mobilization of H^+ and toxic monomeric Al. Hence these internal S sources need to be taken into account not only in understanding watershed S biogeochemistry, but also in applying various management tools such as critical loads (Sverdrup and de Vries, 1994; Dupont et al., 2005; Ouimet et al., 2006) for predicting the effects of changing atmospheric deposition on ecosystem responses.

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Table 1. Northeastern US and southeastern Canadian watersheds used in sulfur budget analyses.

Watershed	Short Name	Location	Latitude	Longitude	Size (ha)	Soil Type	Dominant Vegetation	Selected References
Biscuit Brook	Biscuit	Catskill Mountains, New York, USA	41.98	-74.5	959	Dystrudept and Fragiudept Inceptisols	<i>Acer rubrum</i> , <i>Fagus grandifolia</i> , <i>Acer saccharum</i> , <i>Betula Alleghaniensis</i>	Stoddard and Murdoch, 1991; Murdoch and Shanley, 2006
Cone Pond	Cone	White Mountains, New Hampshire, USA	43.9	-71.6	33.4	Typic and Lithic Haplorthods	<i>Picea rubens</i> , <i>Abies balsamea</i> , <i>Tsuga canadensis</i> , <i>F. grandifolia</i> , <i>A. saccharum</i>	Bailey et al., 2004; Mitchell et al., 2008
HBEF-W6	HBEF	White Mountains, New Hampshire, USA	43.93	-71.75	13.2	Typic and Lithic Haplorthods	<i>A. saccharum</i> , <i>F. grandifolia</i> , <i>B. allegheniensis</i> , <i>A. balsamea</i> , <i>P. rubea</i>	Likens and Bormann, 1995; Likens et al. 1990, 2002
Arbutus	Arbutus	Adirondack Mountains, New York, USA	43.98	-74.23	352	Uplands: Becket-Mundal (coarse-loamy, mixed, frigid typic Haplorthods); Wetlands: Greenwood Mucky peats	<i>F. grandifolia</i> , <i>A. saccharum</i> , <i>T. canadensis</i>	Mitchell et al., 2001b, 2006
Mersey Watershed	Mersey	Kejimikujik National Park, Nova Scotia, Canada	44.42	-65.23	29500	Uplands are shallow podsols with gleysols and fens and peat bogs	<i>P. glauca mariana</i> , <i>A. balsamea</i> , <i>Pinus strobus</i> , <i>T. canadensis</i> , <i>A. saccharum</i> ; <i>B. papyrifera</i> , <i>F. grandifolia</i>	Yanni et al., 2000
Moosepit Watershed	Moosepit	Kejimikujik National Park, Nova Scotia, Canada	44.42	-65.23	1700	Upland are shallow podsols composed of granitic and quartzite materials. In areas of poor drainage, gleysols and fens and peat bogs.	<i>P. glauca mariana</i> , <i>A. balsamea</i> , <i>P. strobus</i> , <i>T. canadensis</i> , <i>A. saccharum</i> , <i>B. papyrifera</i> ; <i>Fagus grandifolia</i>	Yanni et al., 2000
Sleepers River, Watershed 9	Sleepers	Vermont, USA	44.48	-72.17	40.5	Typic Dydrudepts (40%), Humic Dydrudepts(20%), Aquic Dystric Eutrudepts (%20), Typic Humaquepts (%20)	<i>A. saccharum</i> , <i>B. alleghaniensis</i> , <i>Fraxinus americana</i>	Shanley et al., 2004, 2005, 2008
Bear Brook (East)	Bear	Maine, USA	44.87	-68.1	10.3	Typic Haplorthods	<i>F. grandifolia</i> , <i>A. rubrum L.</i> , <i>A. saccharum</i> , <i>B. alleghaniensis</i> , <i>P. rubens</i>	David et al.,1990; Stam et al., 1992; Norton and Fernandez, 1999

Table Continued.

Plastic Lake (PC1)	Plastic	Ontario, Canada	45.18	-78.83	23.3	acidic podsols in uplands, organic soils and gleysols in depressions and wetlands	<i>Pinus strobus</i> , <i>Tsuga canadensis</i> , <i>Quercus rubra</i> , <i>Thuja occidentalis</i> , <i>Picea mariana</i>	Dillon and LaZerte, 1992; LaZerte 1993; Devito 1995.
Harp Lake (HP3A)	Harp	Ontario, Canada	45.38	-79.12	3.7	acidic podsols in uplands, organic soils and gleysols in depressions and wetlands	<i>Acer saccharum</i> , <i>Acer rubrum</i> , <i>Populus grandidentata</i> , <i>Fagus grandifolia</i>	Eimers and Dillon, 2002; Eimers et al., 2004b
Hermine	Hermine	Quebec, Canada	45.98	-74.02	5.1	sandy orthic or gleyed ferro-humic and humo-ferric podsols or Cryorthods	<i>A. saccharum</i> , <i>F. grandifolia</i> , <i>B. alleghaniensis</i>	Biron et al., 1999; Bélanger et al., 2002; Courchesne et al., 2005
Lake Clair	Clair	Centre récréotouristique de Duchesnay, Quebec, Canada	46.95	-71.67	226	Entic Haplorthod or Ferro-Humic Podzol	<i>Acer saccharum</i> , <i>Fagus grandifolia</i> , <i>Betula alleghaniensis</i>	Houle et al., 1997
Lake Laflamme	Laflamme	Réserve faunique des Laurentides, Quebec, Canada	47.3281	-71.126944	68	Typic Haplorthods or Orthic Humo-Ferric Podzol	<i>Abies balsamea</i> , <i>Picea glauca</i> , <i>Betula papyrifera</i>	Houle and Carignan 1992, 1995 ; Houle et al., 2001
Turkey Lakes (average of watersheds 31-35, 37-39, 42, 46-47, 49-50)	Turkey	Ontario, Canada	47.05	-84.4	3 to 115	Uplands: Haplohumods and Haplorthods; Wetland: Haplohemists	<i>A. saccharum</i> (90%) <i>B. alleghaniensis</i> , <i>P. strobus</i> , <i>P. glauca</i>	Beall et al., 2001; Jeffries et al., 1988
Lake Tirasse	Tirasse	Réserve faunique Ashuapmushuan, Quebec, Canada	49.75	-73.01	56	Typic Haplorthods or Orthic Humo-Ferric Podzol	<i>P. mariana</i> , <i>P. banksiana</i>	Duchesne and Houle, 2006

Table 2. Watershed data utilized in sulfur budget calculations (1985 - 2002)

Watershed	Period of record for each site within study period	Precipitation collection method (Bulk or Wet Only)	Discharge measurements intervals	Discharge chemistry measurement intervals
Biscuit Brook	1985-2002	Wet Only (NADP)	15 minutes	Weekly + Events
Cone Pond	1985-2002	Bulk	Continuous	Weekly +
HBEF	1985-2002	Bulk	Continuous	Weekly
Arbutus	1985-2002	Wet Only (NADP)	15 minutes	Weekly
Mersey	1985-2002	wet only	Continuous	Weekly
Moosepit	1985-2002	wet only	Continuous	Weekly
Sleepers River	1992-2002	Bulk	5 min	Weekly + Events
Bear Brook	1985-2001	Wet Only	5 minutes	Weekly
Plastic Lake	1985-1997	Bulk	10 minutes	Weekly + Events)
Harp Lake	1985-1997	Bulk	10 minutes	Weekly + Events
Hermine	1995-1997, 2001-2002	Bulk	Daily	Daily
Lake Clair	1985-2002	Bulk	Read every 5 seconds/1 hour average recorded	Weekly
Lake Laflamme	1985-1996, 1999-2002	Wet Only	Read every 5 seconds/1 hour average recorded	Weekly
Turkey Lakes ¹	1985-2002	Wet only	Continuous	Daily during peak melt, Bi-weekly remainder of year

Table Continued.

Lake Tirasse	1997-2002	Bulk	Read every 5 seconds/1 hour average recorded	Weekly
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¹Mean values of Discharge for watersheds 31, 32, 33, 34, 35, 37, 38, 39, 42, 46, 47, 49, 50

Table 3. Temporal Changes (Annual Values) for Precipitation and Discharge from 1985 through 2002 (**Significant values $p \leq 0.05$**)

Watershed	Precip. Flux kg S ha⁻¹ yr⁻¹	p value	Precip. Conc. μmol SO₄²⁻ L⁻¹ yr⁻¹	p value	Discharge Conc. p value μmol SO₄²⁻ L⁻¹ yr⁻¹
Biscuit Brook	-0.28	0.0003	-0.61	0.0001	-1.29 <.0001
Cone Pond	-0.16	0.0276	-0.19	0.3201	-0.60 0.1401
HBEF	-0.17	0.0130	-0.39	0.0002	-0.81 <.0001
Arbutus	-0.18	0.0002	-0.58	<.0001	-0.86 0.0142
Mersey Watershed	-0.14	0.0011	-0.35	0.0015	0.08 0.481
Moosepit Watershed	-0.14	0.0011	-0.35	0.0015	0.05 0.6398
Sleepers River	0.06	0.6357	-0.04	0.8768	-0.02 0.9734
Bear Brook	-0.07	0.3161	-0.09	0.4945	-1.24 0.2489
Plastic Lake	-0.22	0.0031	-0.68	0.0007	-3.45 0.0557
Harp Lake	-0.22	0.0031	-0.68	0.0007	-2.08 0.0083
Hermine	-0.05	0.5519	0.09	0.6294	3.00 0.3528
Lake Clair	-0.24	0.0423	-0.34	0.1546	-0.79 <.0001
Lake Laflamme	-0.12	0.0347	-0.21	0.0771	-1.18 <.0001
Turkey Lakes	-0.21	0.0004	-0.41	0.0004	-0.72 0.0084
Lake Tirasse	-0.07	0.5748	-0.27	0.5162	-0.59 0.0078

Table 4.

Discrepancies calculated using $\mu\text{mol SO}_4^{2-}$ concentrations and the volume of discharge for, precip + Equation 2 or precip + Equation 3 ($p \leq 0.05$)

Site	Slope Annual Precip (mm) versus conc. discrepancy (Precip. + Equation 2)	P value	Slope Annual Precip (mm) versus conc. discrepancy (Precip. + Equation 3)	P value
Arbutus	-0.065	0.008	-0.078	0.005
Biscuit Brook	-0.016	0.015	-0.021	0.006
Cone Pond	-0.028	0.007	-0.037	0.002
Harp	-0.066	0.013	-0.089	0.003
HBEF	-0.019	<.0001	-0.024	<.0001
Mersey	-0.015	0.037	-0.019	0.017
Moosepit	-0.012	0.027	-0.016	0.007
Turkey Lakes	-0.029	0.019	-0.039	0.004

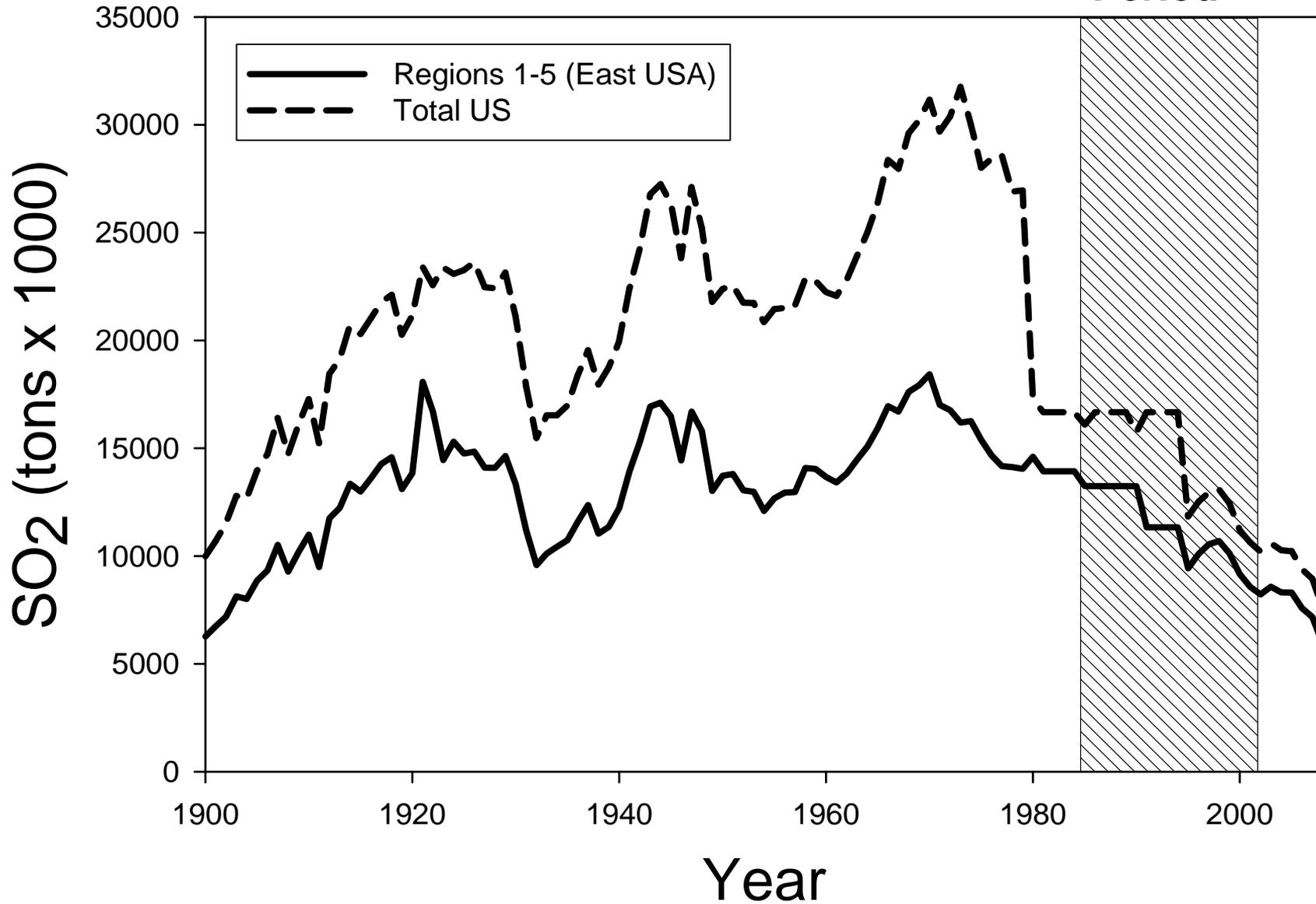
LIST OF FIGURES

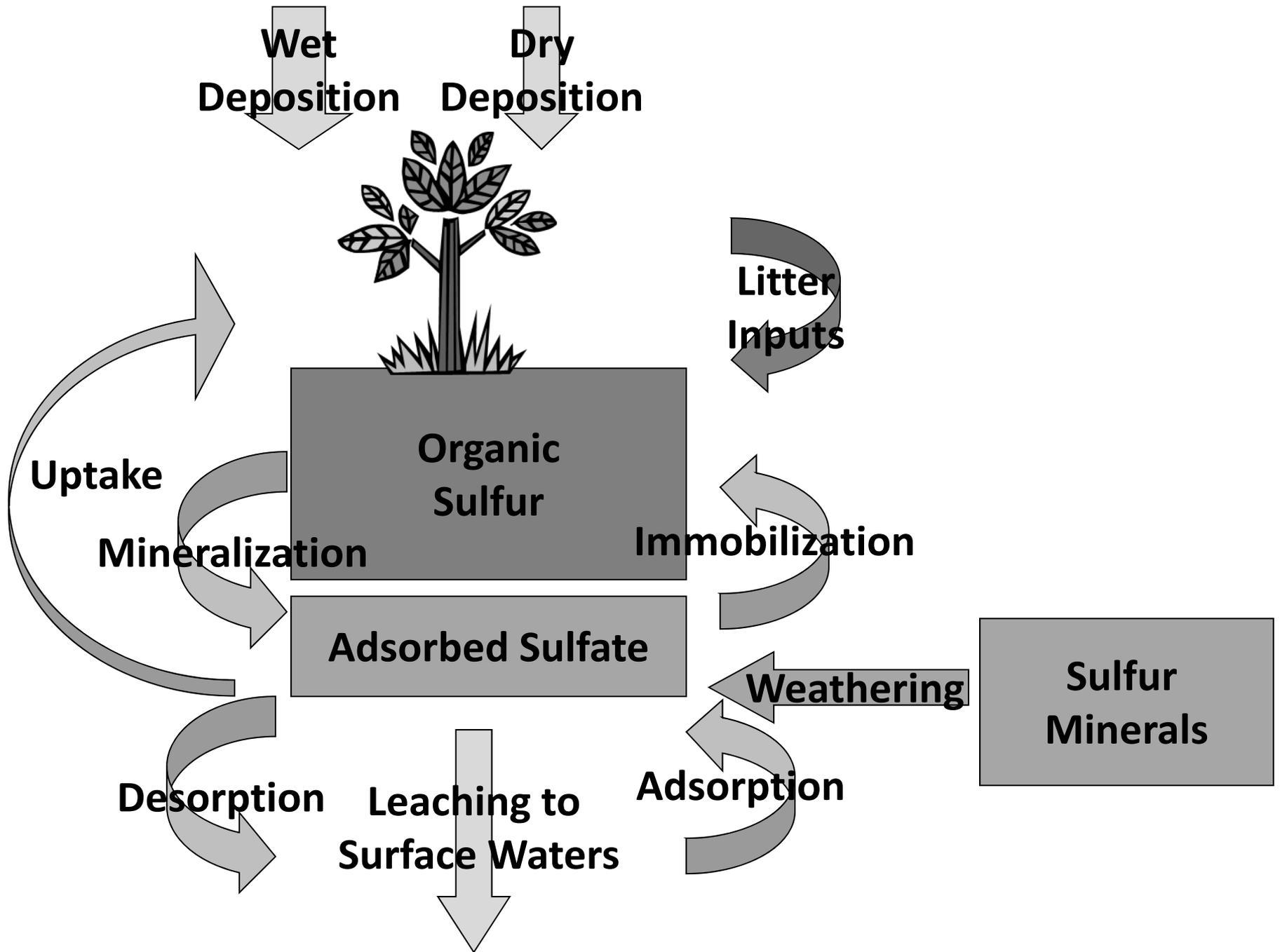
1. SO₂ emissions for entire United States and Regions 1-5 (eastern U.S.) from 1900 to 2008. Source of information is provided in the text.
2. Major sulfur pools and fluxes in a forested watershed.
3. Location of watersheds in the northeastern U.S. and southeastern Canada with information on sulfur budgets and location of CASTNET and CAPMoN sites used in developing Equation 1.
4. Solid line is regression equation of observed versus predicted annual SO₂ concentrations as a function of latitude, longitude and SO₂ emissions from the eastern United States for CASTNET and CAPMoN sites. Dashed lines are 95% confidence limits. Sites used in these calculation are shown in Figure 3.
5. Range and mean values of calculated SO₂ concentrations for the period from 1985 to 2002 using formulation based upon latitude, longitude and eastern U.S. SO₂ emissions for the study sites (see text for details).
6. Predicted SO₂ concentrations for study region for CMAQ model, AURAMS model, and Equation 1 for year 2002.
7. Calculated relationships between annual SO₂ concentrations and total dry deposition of S using data for CASTNET (Equation 2) and CAPMoN (Equation 3) sites.
8. Predicted S dry deposition for study region for CMAQ model, AURAMS model, Equation 2 (CASTNET data) and Equation 3 (CAPMoN data) for year 2002.
9. Mean annual precipitation, discharge values and calculated evapotranspiration (precipitation - discharge) for each watershed for the period from 1985 through 2002. For details on data utilized see Table 1.
10. Annual fluxes of total atmospheric sulfur deposition (precipitation combined with estimates of dry deposition based upon equations 2 or 3, see text for details) with discrepancy calculated by subtracting sulfur in discharge from the estimates of total atmospheric sulfur deposition.

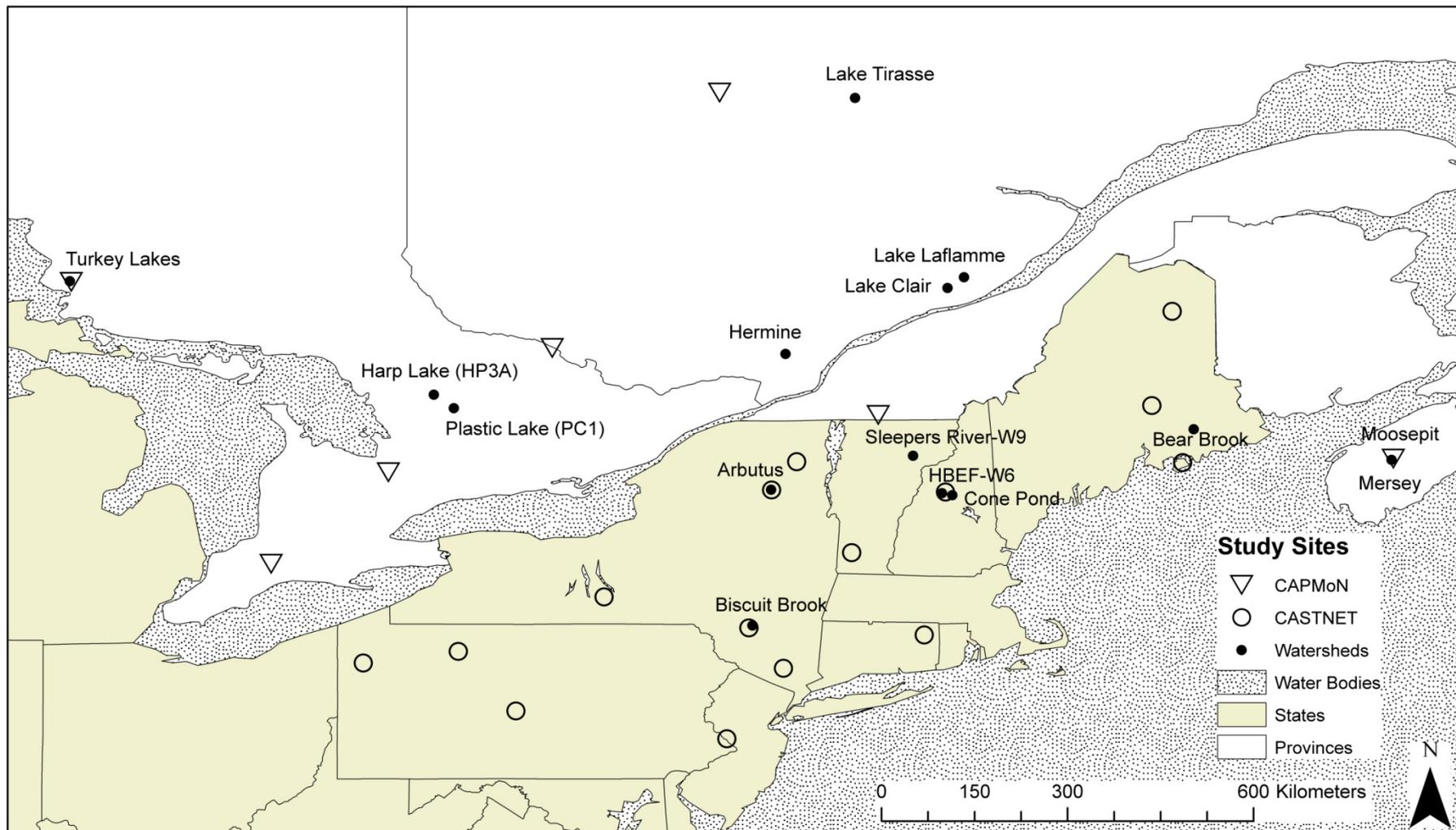
11. Annual sulfur budgets for Hubbard Brook Watershed 6: bulk precipitation + either Equation 2 or Equation 3 dry deposition estimates, discharge and discrepancy using Equation 2 or Equation 3 deposition estimates.
12. Annual sulfur budgets for Turkey Lakes watersheds: bulk precipitation + either Equation 2 or Equation 3 dry deposition estimates, discharge (average of watersheds as detailed in text) and discrepancy using either Equation 2 or Equation 3 deposition estimates.
13. Annual hydrology (precipitation and discharge) for Hubbard Brook Watershed 6.
14. Annual hydrology (precipitation and discharge) for Turkey Lakes (Discharge averaged for watersheds as detailed in text).
15. Classification of watersheds based upon the SO_4^{2-} concentration contributed by internal sulfur sources. Error bars are 1 standard error. See text for details on rationale of classification.
16. Mass balance annual discrepancy value in SO_4^{2-} concentrations calculated from the differences in discharge - precipitation + dry deposition from Equation 2 (CASTNET values) (closed circle) and precipitation + dry deposition from Equation 3 (CAPMoN values) (open circle) for Arbutus, Biscuit Brook and Moosepit. See text for further details on the calculations.

SO₂ Emissions Data (EPA)

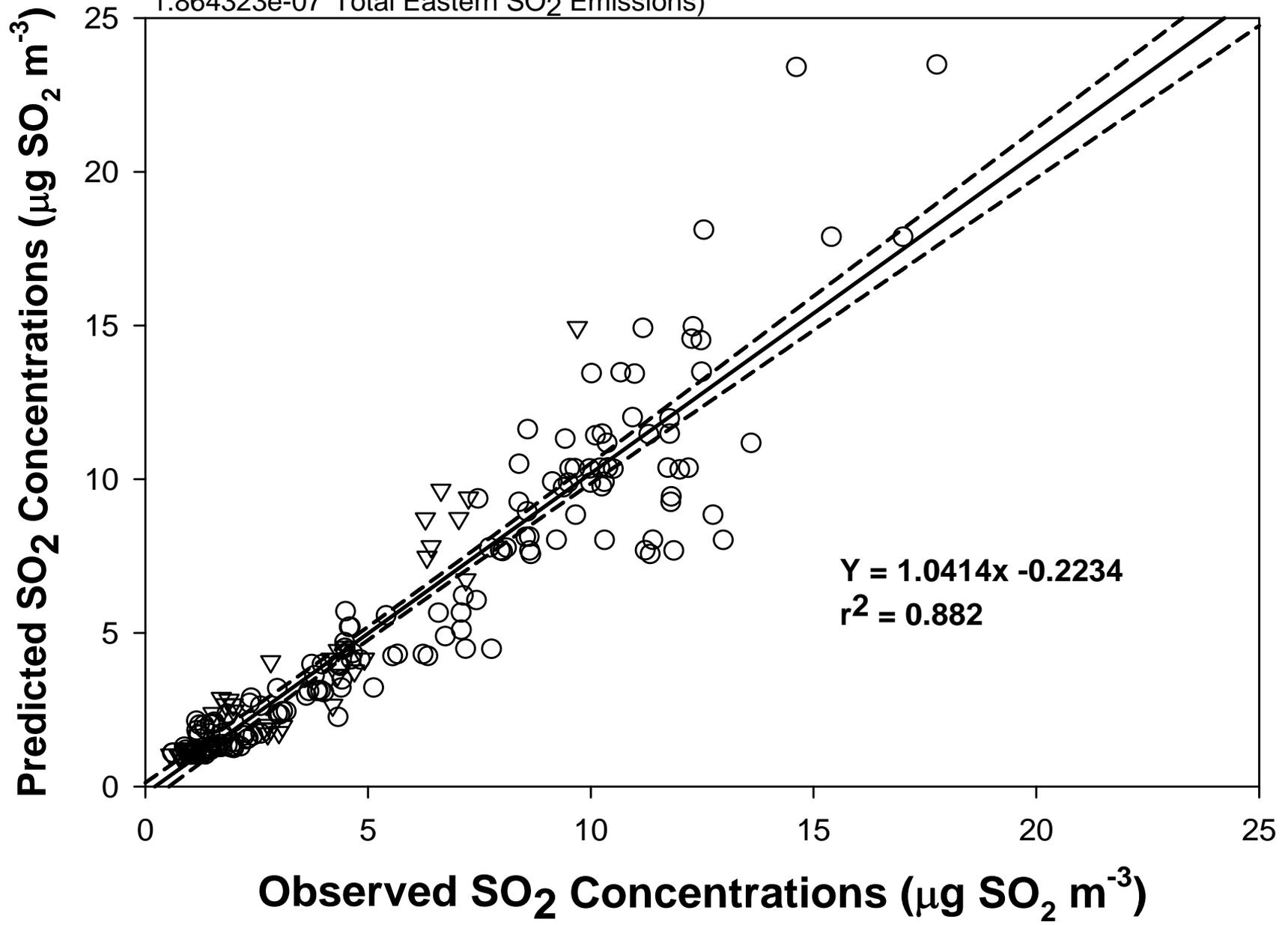
**Study
Period**



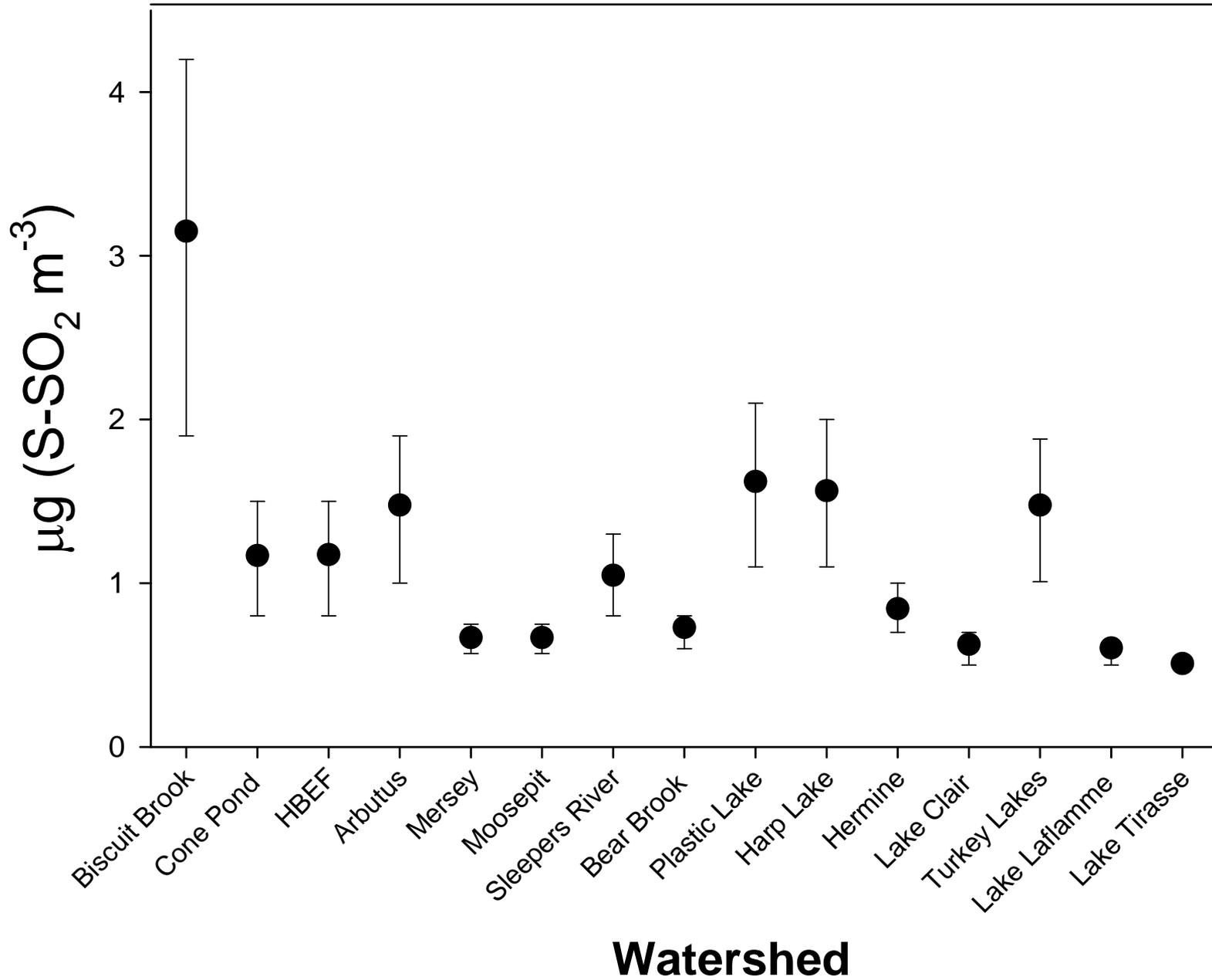




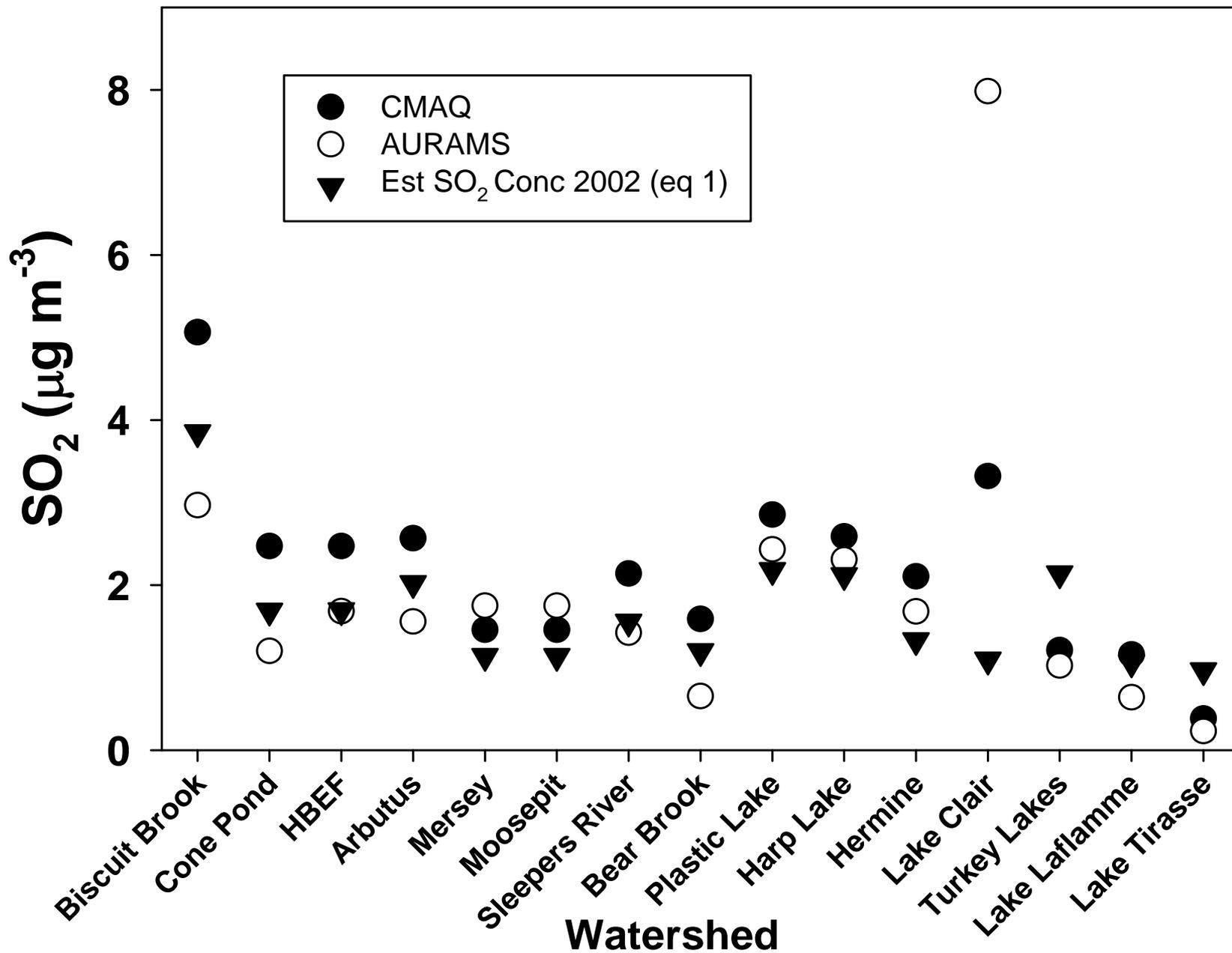
Predicted = 0.9 + exp(7.86697- 0.46330*Latitude + 0.14944*Postive Longitude + 1.864323e-07*Total Eastern SO₂ Emissions)

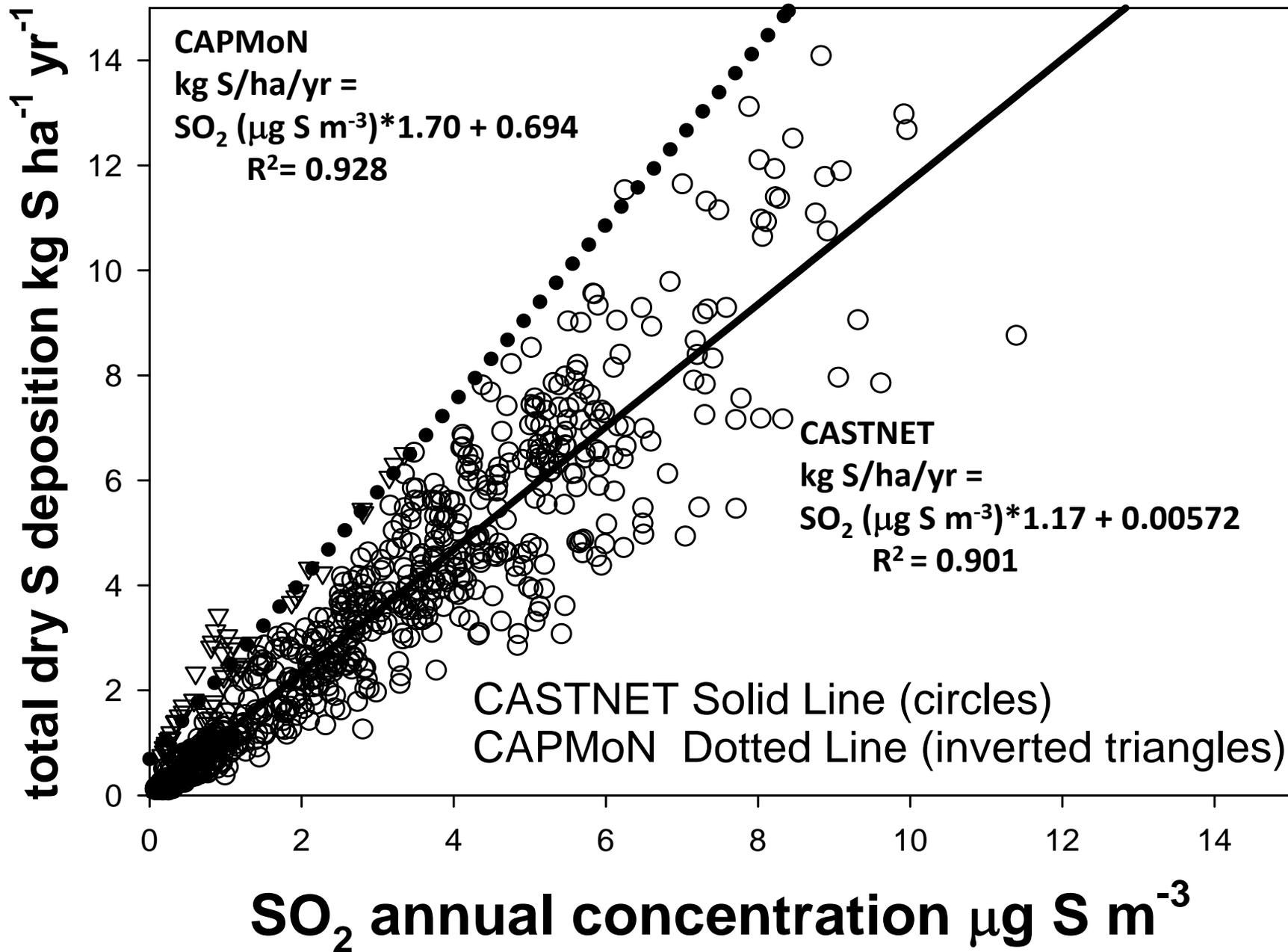


1985-2002

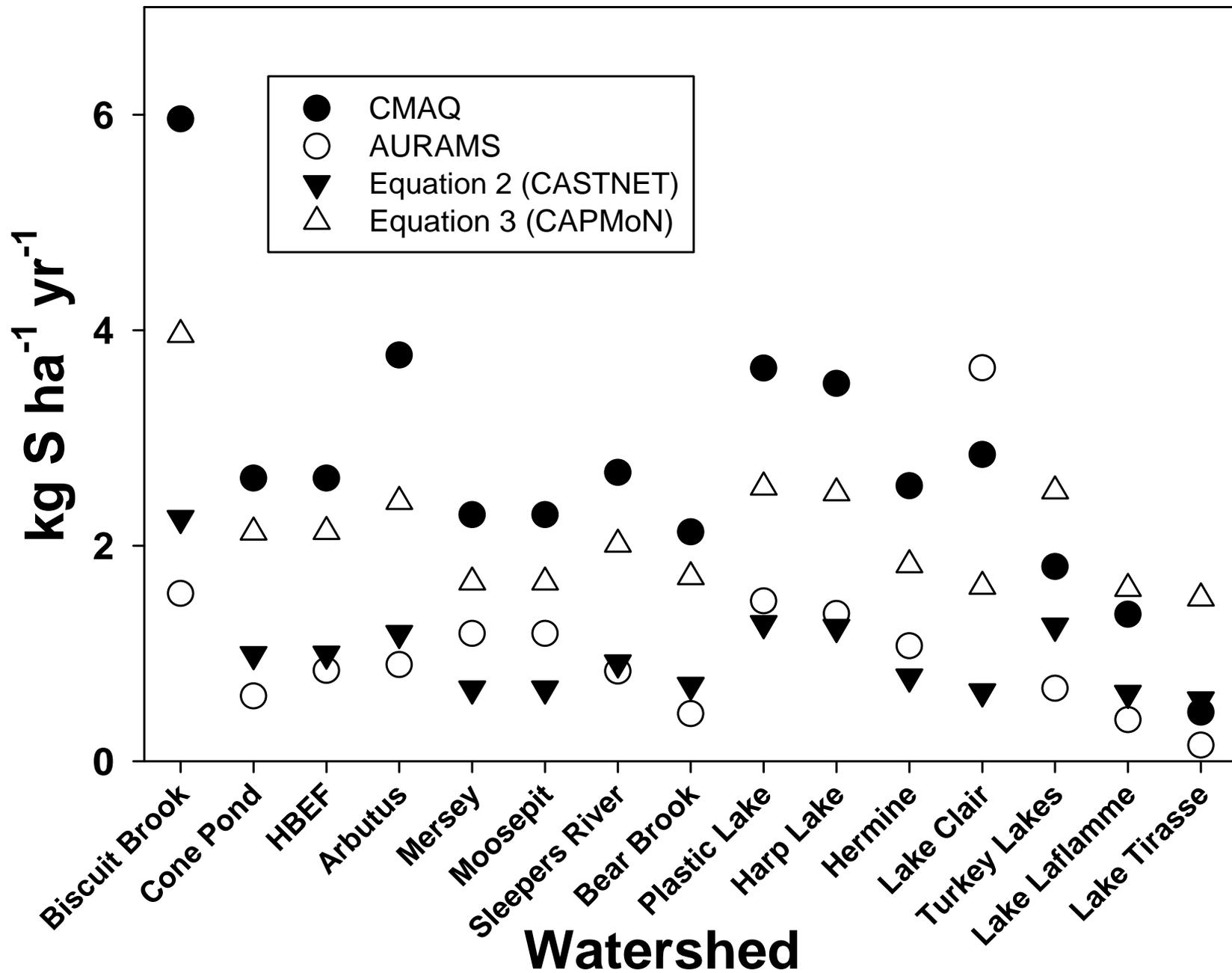


Annual Average for 2002

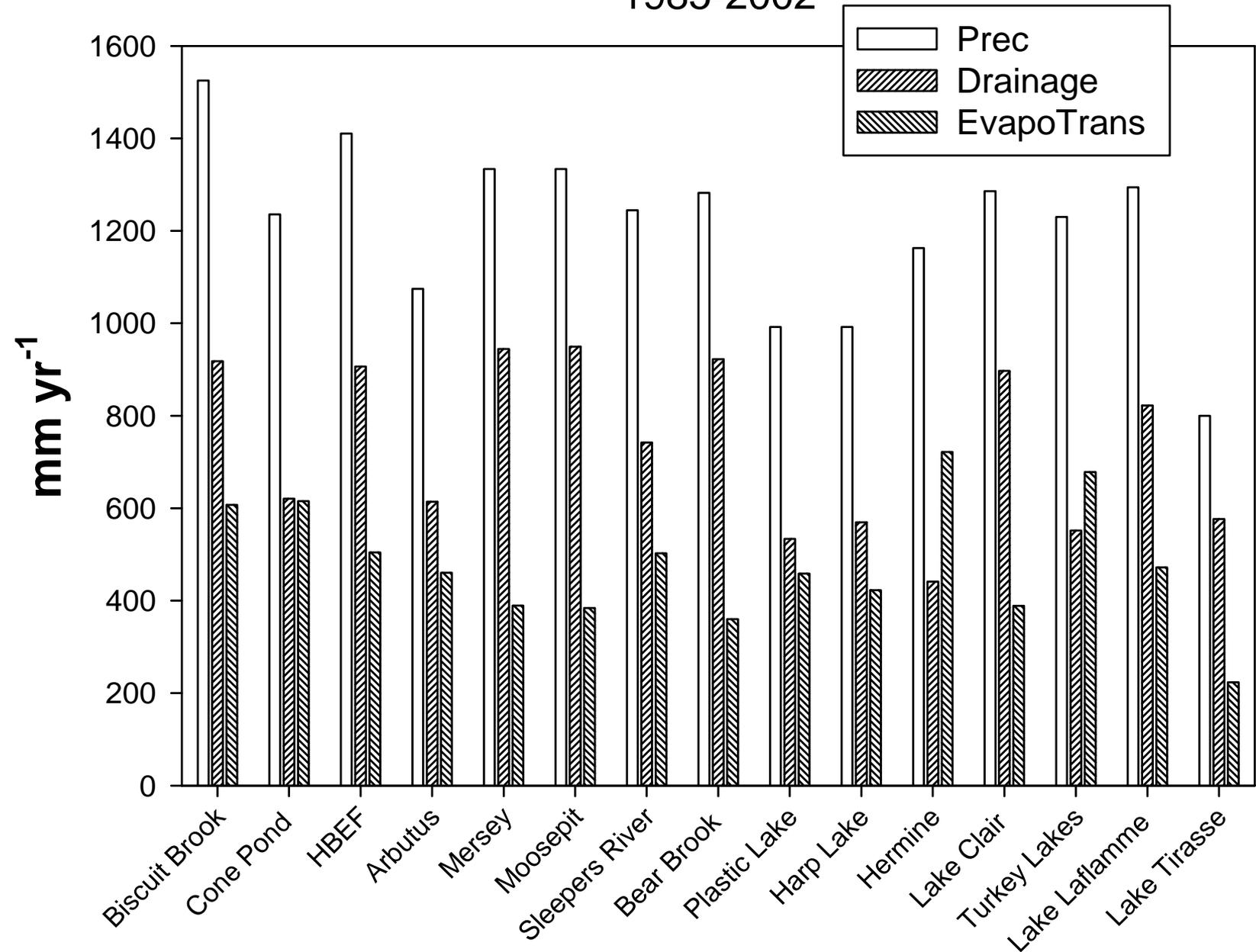




Dry Deposition for 2002

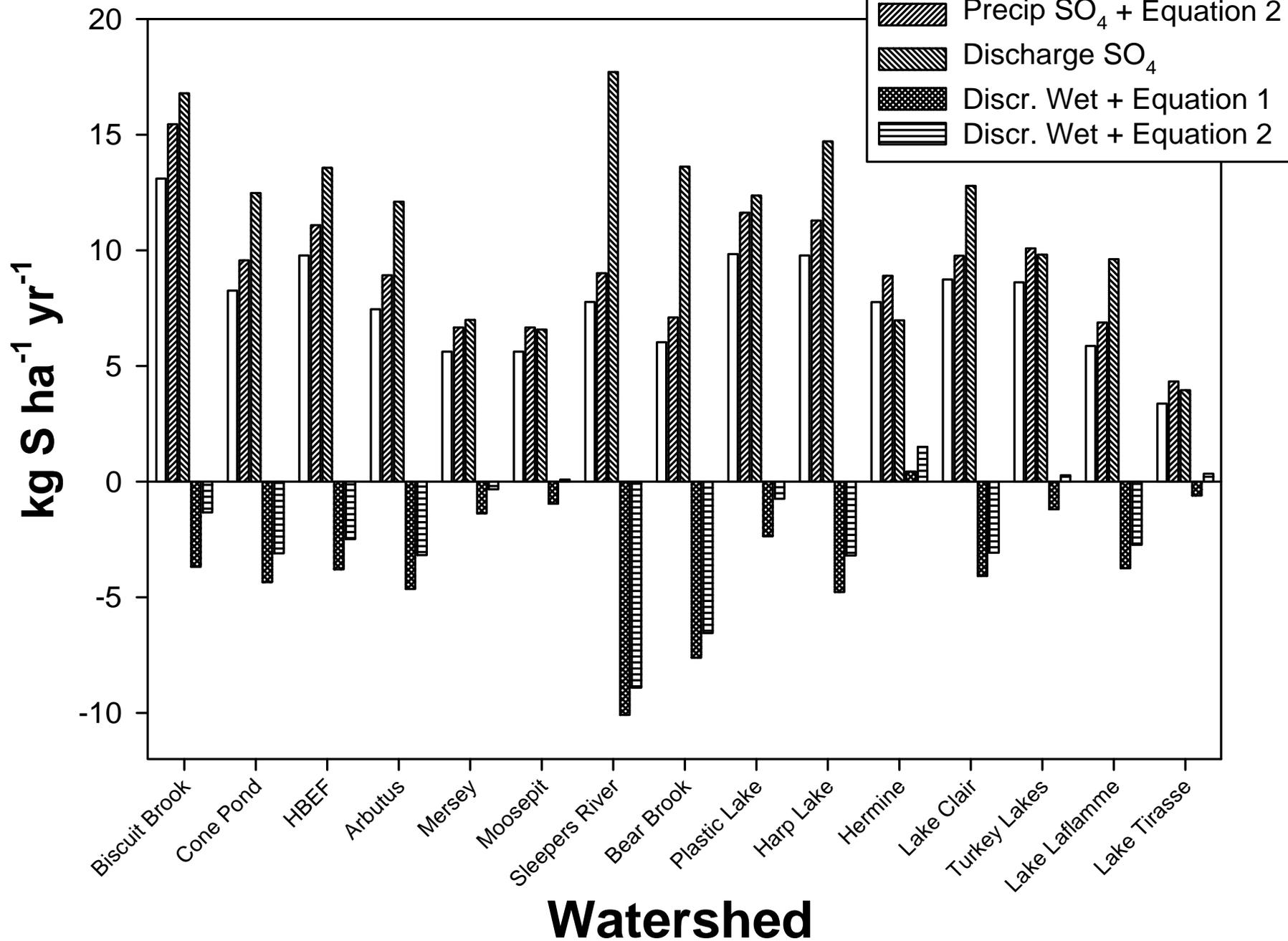


1985-2002

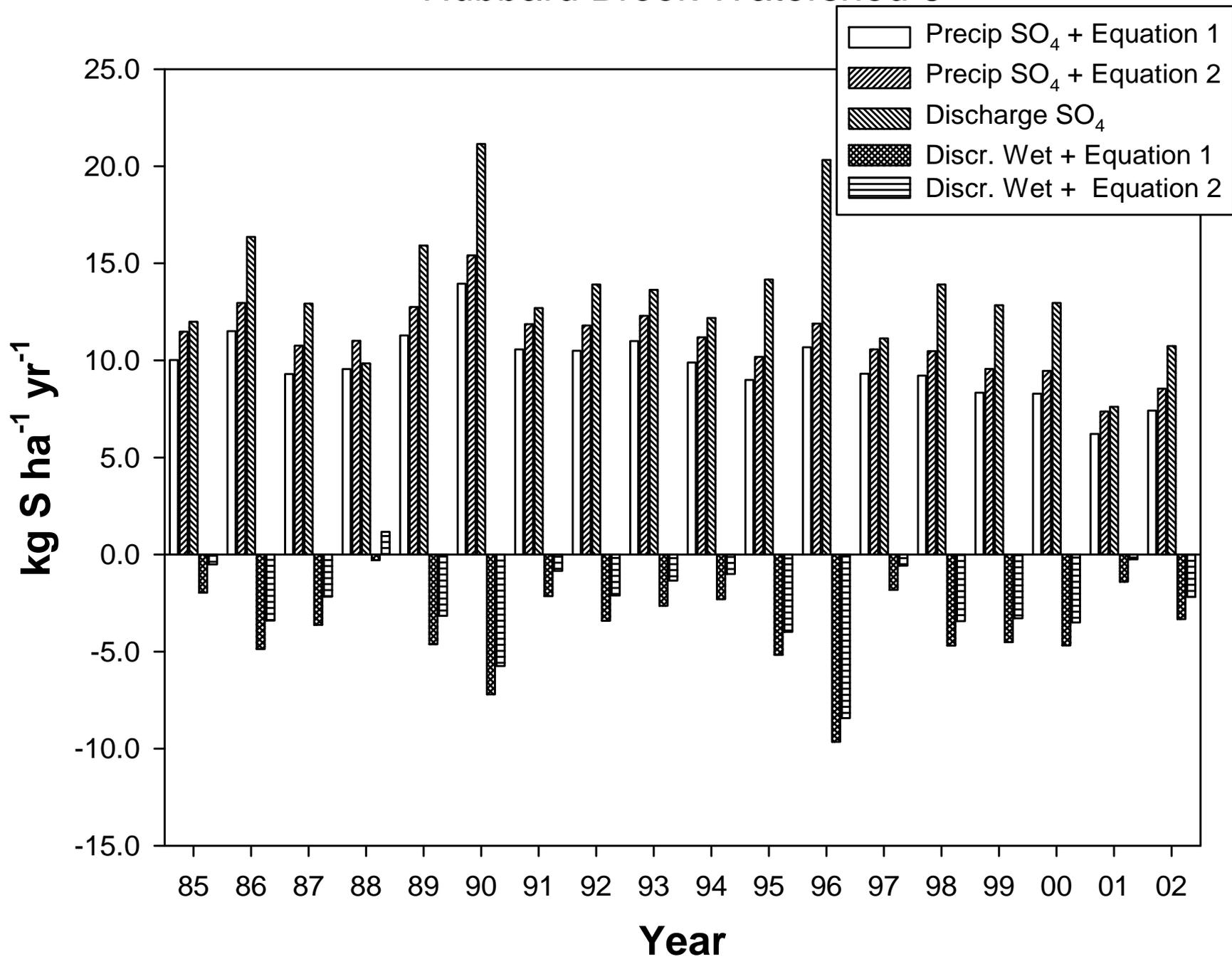


Watershed

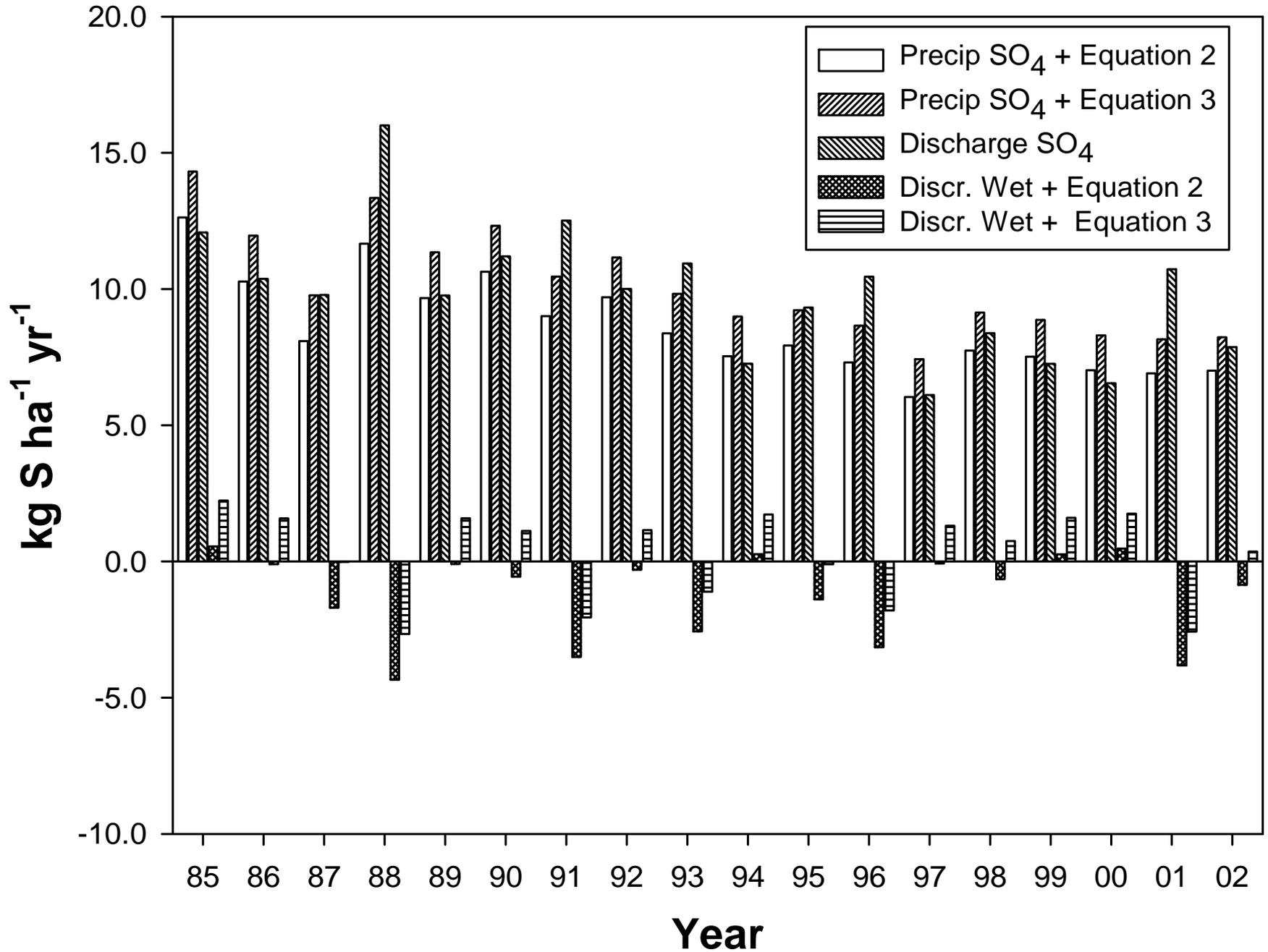
1985-2002



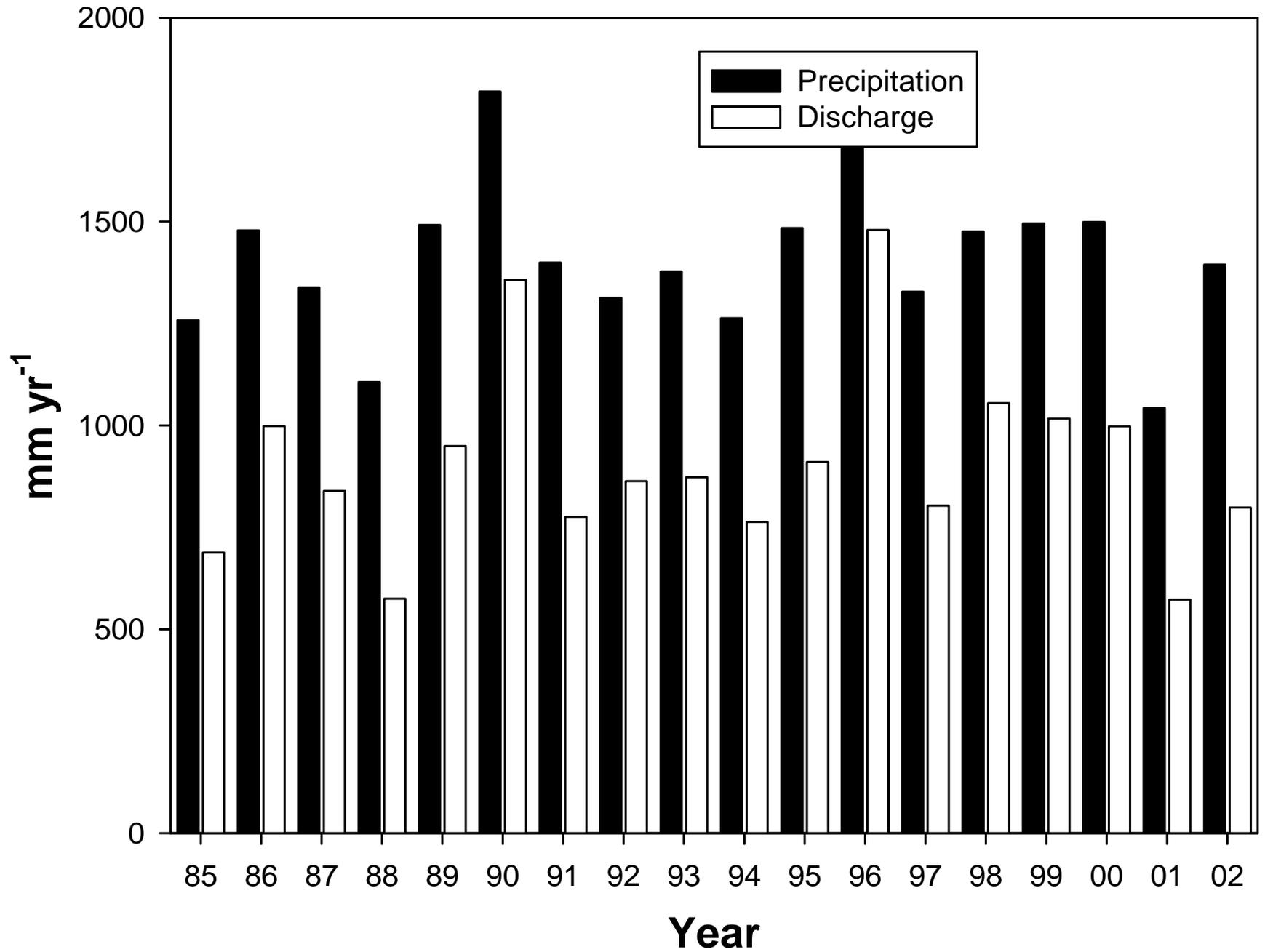
Hubbard Brook Watershed 6



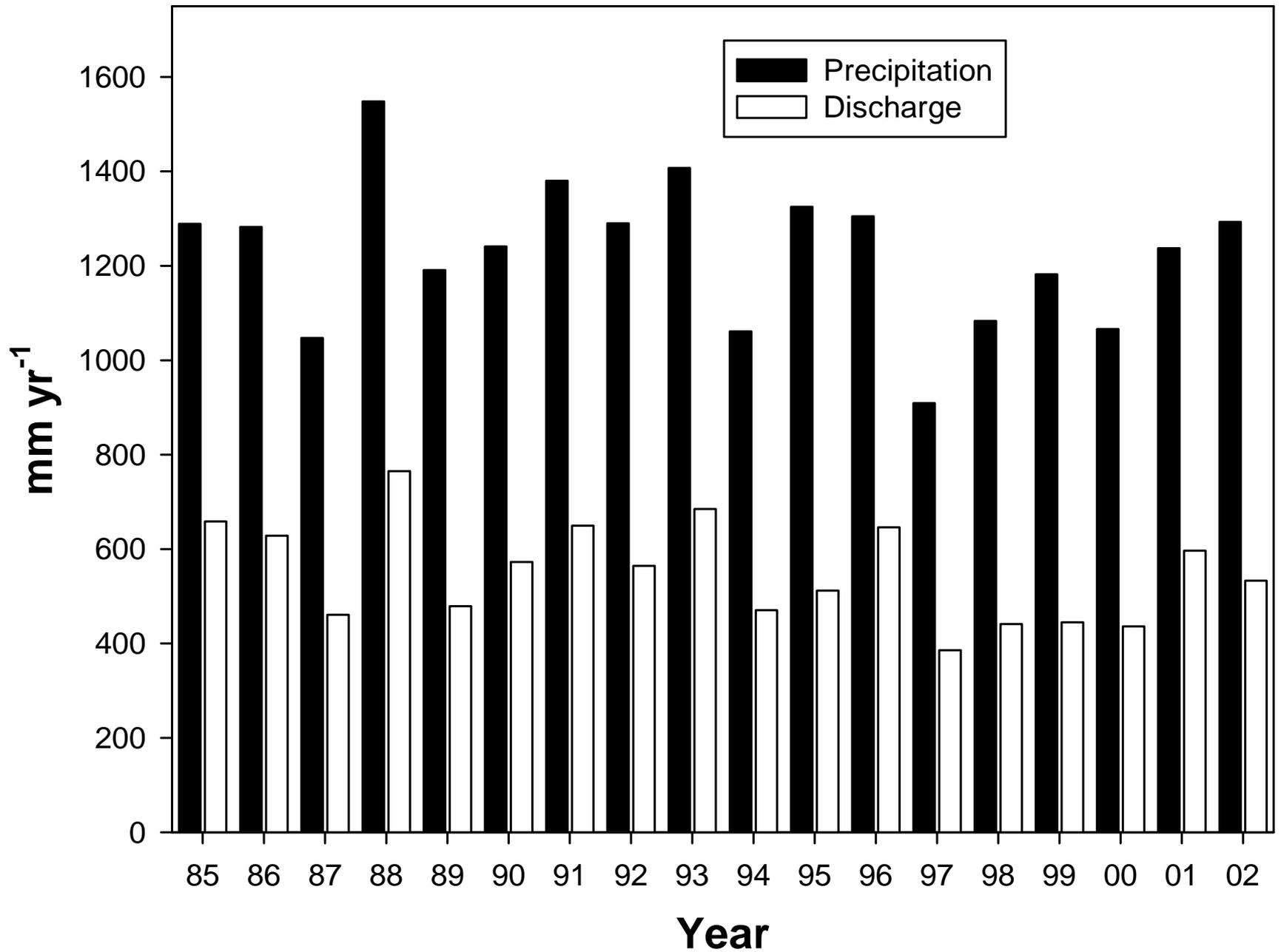
Turkey Lakes



Hubbard Brook Watershed 6



Turkey Lakes



Contribution of Internal S Sources to Drainage Water Sulfate

$\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$

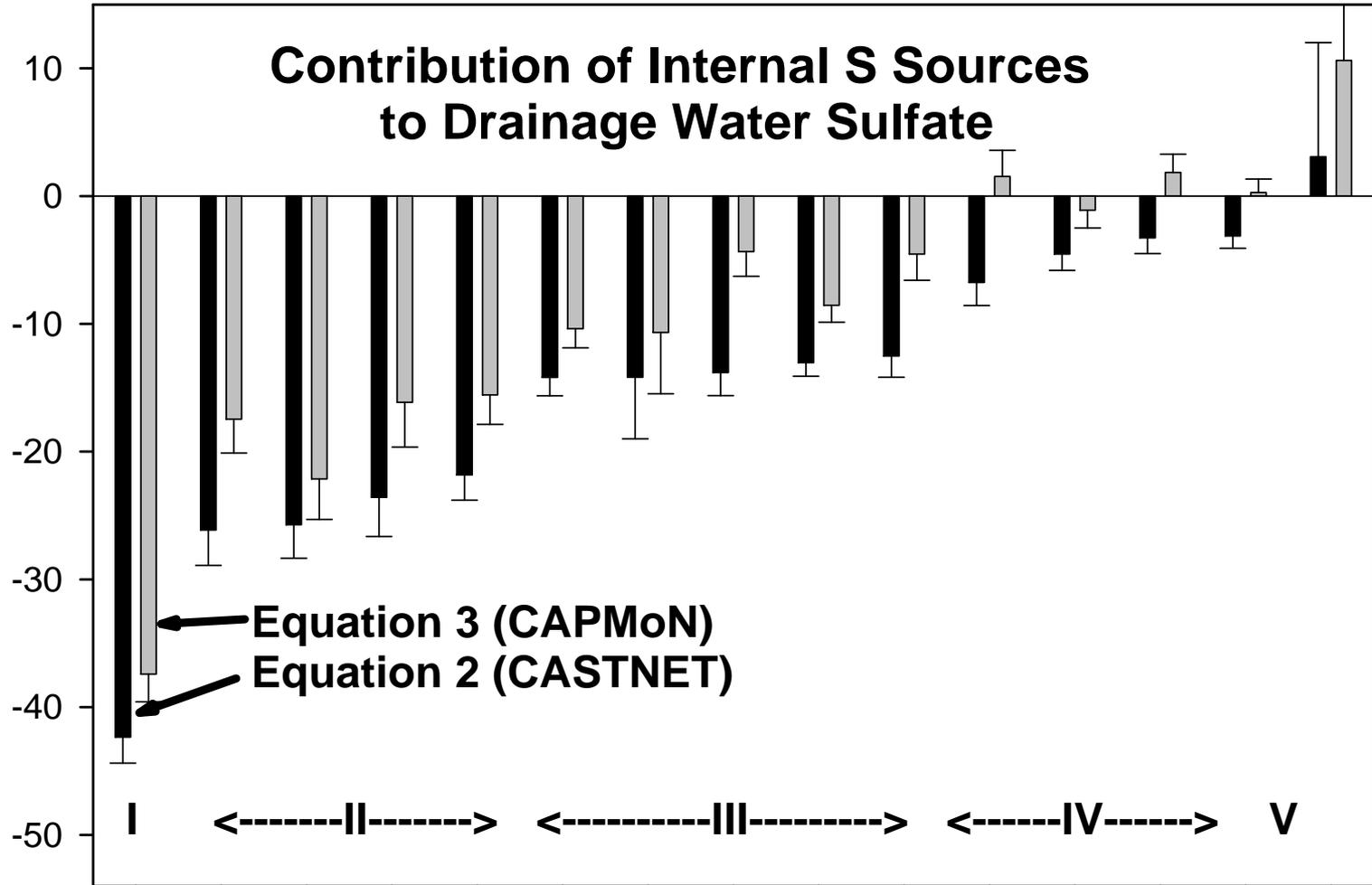
10
0
-10
-20
-30
-40
-50

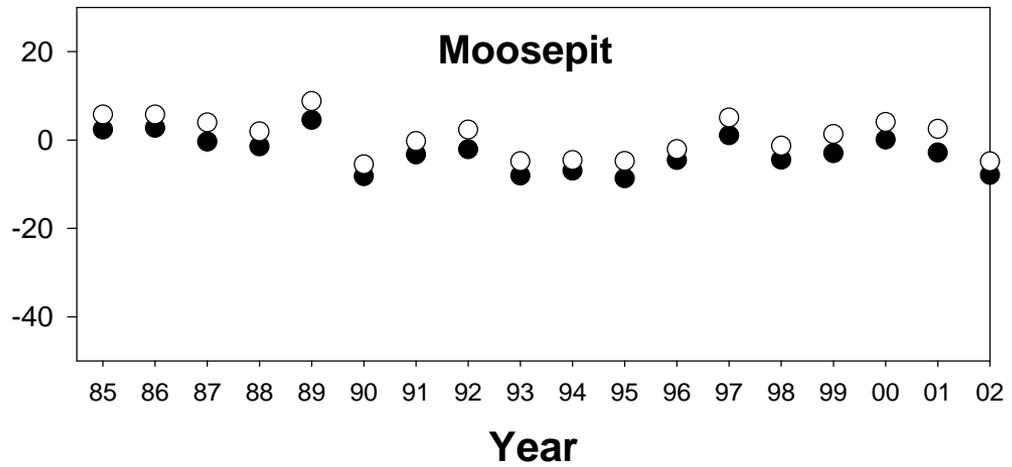
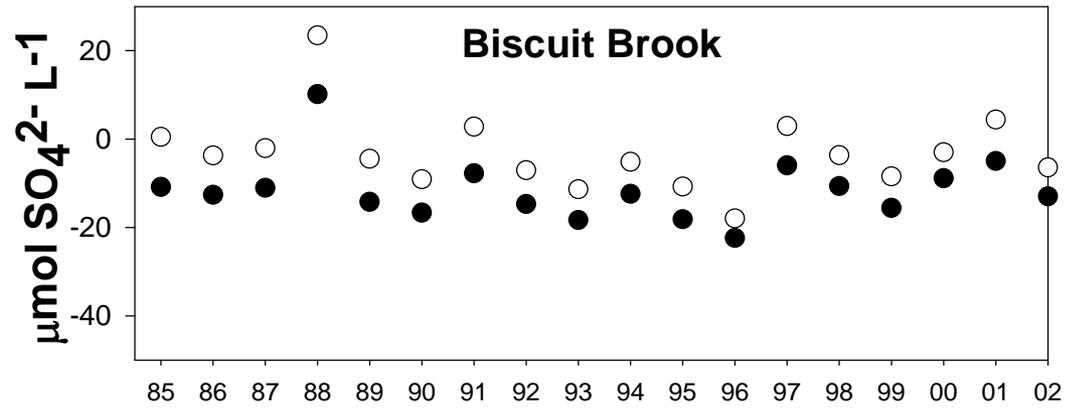
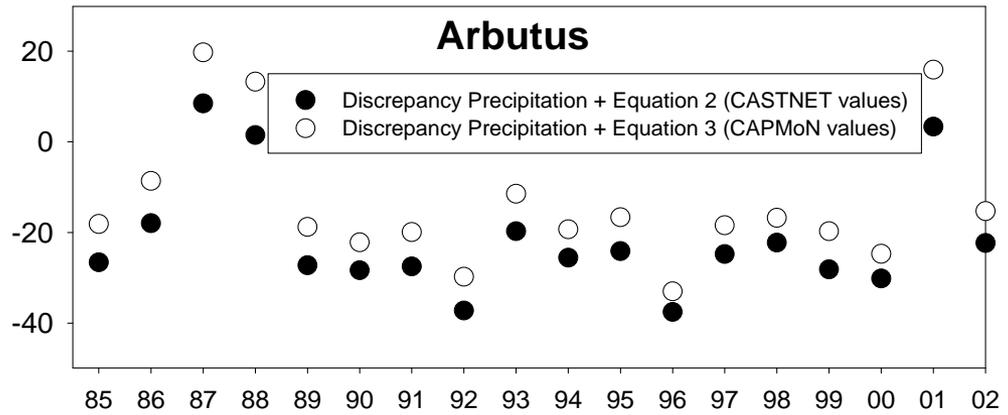
Equation 3 (CAPMoN)
Equation 2 (CASTNET)

Sleepers River
Harp Lake
Bear Brook
Arbutus
Cone Pond
Lake Laflamme
Lake Clair
Plastic Lake
HBEF
Biscuit Brook
Turkey Lakes
Mersey
Lake Tirasse
Moosepit
Hermine

Watershed

I ←-----II-----> ←-----III-----> ←-----IV-----> V





Appendix I

**Supplemental Information on Sulfur Budgets for Individual Watersheds
for the following manuscript published in Biogeochemistry (2010) entitled:**

Comparisons of Watershed Sulfur Budgets in Southeast Canada and Northeast US: New Approaches and Implications

by

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To facilitate the temporal and spatial comparisons of the watersheds, the discrepancies in annual S budgets in $\text{kg S ha}^{-1} \text{ yr}^{-1}$ were converted to mean annual, volume-weighted concentration values ($\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) using the annual stream discharge for each watershed. This conversion to concentrations facilitates comparisons of S budget discrepancies among watersheds and over time since the interannual S drainage water fluxes for each catchment are greatly affected by differences in annual water discharge. The mean annual concentration discrepancies for each site using precipitation plus dry deposition (Equation 2: CASTNET values; Equation 3: CAPMoN values) were determined. An examination of the mean SO_4^{2-} concentration discrepancies suggested that the 15 sites can be categorized into five groups. Sulfur and water budget information for each of these groups and each respective site are provided below.

CATEGORY I

Sleepers River (Watershed 9) in Vermont had a mean annual precipitation (1245 mm yr^{-1}) that was slightly higher than the average of all watershed sites. The S precipitation input ($6.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was close to the average for all sites. Dry deposition values (Equation 2: $1.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $2.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were slightly lower than the average for all watersheds. Using these dry deposition estimates, the watershed S budget discrepancies would be either $-10.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-42.0 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or $-8.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-36.8 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$), respectively, the highest discrepancies of the 15 watershed sites used in the current analyses. The source of this discrepancy has been clearly identified, using mass budgets and stable isotopic analyses of S sources, to be weatherable S minerals (Bailey et al., 2004; Shanley et al., 2005), with possible

occasional contributions from reoxidized secondary sulfides (Shanley et al., 2008).

CATEGORY II

Bear Brook (Watershed East) in Maine had mean annual precipitation (1282 mm yr⁻¹) that was slightly higher than the average of all watershed sites. The precipitation input of S (5.2 kg S ha⁻¹ yr⁻¹) was lower by 1.3 kg S ha⁻¹ yr⁻¹ than the average of all sites. Dry deposition values (Equation 2: 0.9 kg S ha⁻¹ yr⁻¹; Equation 3: 1.9 kg S ha⁻¹ yr⁻¹) were lower by 0.5 kg S ha⁻¹ yr⁻¹ than the average for all watersheds. Using the two equations for dry deposition estimates, the watershed S discrepancies were either -7.6 kg S ha⁻¹ yr⁻¹ (-27.2 μmol SO₄²⁻ L⁻¹) or -6.6 kg S ha⁻¹ yr⁻¹ (-23.4 μmol SO₄²⁻ L⁻¹), respectively. These discrepancies are the third (Equation 2) or second (Equation 3) highest of the 15 watersheds in our study. Bear Brook Watershed East is the reference watershed to Bear Brook Watershed West, the latter of which has been treated since 1989 with (NH₄)₂SO₄ at ~28.8 kg S ha⁻¹ yr⁻¹ and ~25.2 kg N ha⁻¹ yr⁻¹ (Norton and Fernandez, 1999). This chemical manipulation is designed to investigate the effects of increased atmospheric deposition of N and S. Investigations at Bear Brook Watershed have established that organic S dominates the soil S pool (David et al., 1990). Experimental work using “mineral soil bags” has shown that much of the short-term variation and response to S additions were due to changes in adsorbed SO₄²⁻ (David et al., 1990). Previous isotopic analyses (δ³⁴S - SO₄²⁻) suggested for Bear Brook Watershed (East) that most of the SO₄²⁻ in discharge can be attributed to S derived from atmospheric deposition (Stam et al., 1992) and the source of this additional S source was not known. Our current results suggest that further studies on the importance of an internal S source are warranted.

Harp Lake (HP3A) Watershed in Ontario had the same mean annual precipitation and S precipitation input as nearby Plastic Lake (Figure 3). Dry deposition values (Equation 2: 1.8 kg S ha⁻¹ yr⁻¹; Equation 3: 3.3 kg S ha⁻¹ yr⁻¹) were slightly lower by 0.1 and 0.4 kg S ha⁻¹ yr⁻¹, respectively than Plastic Lake due to the predominantly deciduous canopy at HP3A (Yao et al., 2009) compared with the coniferous forest at PC1. Using these estimates, the watershed S discrepancies would be either -4.8 kg S ha⁻¹ yr⁻¹ (-24.8 μmol SO₄²⁻ L⁻¹) or -3.2 kg S ha⁻¹ yr⁻¹ (-15.7 μmol SO₄²⁻ L⁻¹), respectively, and hence substantially greater than nearby Plastic Lake (Figure 3). In contrast to Plastic Lake Watershed (PC1), the HP3A inflow to Harp Lake (Eimers et al., 2008; Seip et al., 1985) is predominantly upland, and as a consequence SO₄²⁻ concentrations in stream water are much less variable over time and the catchment S budget is consistently negative. More details on the role of wetlands are provided below for the section on Plastic Lake.

Arbutus Watershed in the Adirondack Mountains of New York had mean annual precipitation (1075 mm yr⁻¹) that was lower than the average of all watershed sites. The S precipitation input (5.7 kg S ha⁻¹ yr⁻¹) was lower by 0.8 kg S ha⁻¹ yr⁻¹ than the average of all sites. Dry deposition values (Equation 2: 1.7 kg S ha⁻¹ yr⁻¹; Equation 3: 3.2 kg S ha⁻¹ yr⁻¹) were somewhat higher than the average for all watersheds (Equation 2: 1.4 kg S ha⁻¹ yr⁻¹; Equation 3: 2.7 kg S ha⁻¹ yr⁻¹). Using these dry deposition estimates, the watershed S discrepancies would be either -4.6 kg S ha⁻¹ yr⁻¹ (-21.5 μmol SO₄²⁻ L⁻¹) or -3.2 kg S ha⁻¹ yr⁻¹ (-13.8 μmol SO₄²⁻ L⁻¹), respectively. Previous analyses also recognized these discrepancies (e.g., Mitchell et al., 2001b). An analysis that included site based estimates of dry deposition suggested that an internal S source was required to balance the S budget for Arbutus Watershed (Park et al., 2003). These discrepancies are,

however, somewhat higher (0.7 to $0.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) than those at the Hubbard Brook Experimental Forest and this higher value would be consistent with the findings based upon SO_4^{2-} isotopic evidence ($\delta^{18}\text{O}$ and $\delta^{34}\text{S}$) (Campbell et al., 2006) and spatial patterns of SO_4^{2-} concentrations (Piatek et al., 2009) that some subcatchments of the Arbutus Watershed have a S mineral weathering source. Summer storm events following periods of drought can result in substantial increases in SO_4^{2-} concentrations, although these increases do not have a major impact on the overall amount of SO_4^{2-} lost through drainage waters (Mitchell et al., 2006, 2008).

Cone Pond Watershed in the White Mountains of New Hampshire had mean annual precipitation (1236 mm yr^{-1}) that was similar (1215 mm yr^{-1}) to the average of all 15 watershed sites. The wet only deposition ($6.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was also similar to the average of all sites ($6.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$). However, dry deposition values (Equation 2: $1.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $2.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were substantially higher than the average for all watersheds. There were substantial discrepancies in the S budget (-4.3 and $-3.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, -20.3 and $-13.7 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$, respectively). Previous work at Cone Pond has suggested the potential importance of a fire in 1820 that heavily burned 85% of the watershed. It has been suggested that the effect of this fire in the reduction of watershed organic matter content has enhanced N retention (Campbell et al., 2004) and dampened SO_4^{2-} mobilization during rewetting following a drought (Mitchell et al., 2008).

CATEGORY III

Lake Laflamme Watershed in Quebec had mean annual precipitation (1294 mm yr^{-1}) that was

similar to nearby Lake Clair. Despite very similar amounts of precipitation, the S precipitation input ($5.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) represented only 65% of the S precipitation at Lake Clair which is closer to pollution sources. Dry deposition values (Equation 2: $0.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $1.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were similar to Lake Clair. Using these dry deposition estimates, the watershed S discrepancies would be either (Equation 2) $-3.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-13.8 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or (Equation 3) $-2.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-9.9 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$), respectively. Between 1999 and 2005, deposition of SO_4^{2-} significantly decreased, resulting in an important reduction in H^+ concentration (Duchesne and Houle 2008). Sulfate also significantly decreased within the soil solution during the same period. Observations indicated that soil SO_4^{2-} sorption should adjust rapidly (within 4 years) to changing S loads and that desorption alone cannot explain long-term net SO_4^{2-} losses (Houle and Carignan, 1995). These observations suggest a net release of SO_4^{2-} from the soil organic reservoirs. An oxygen isotope study of the dissolved SO_4^{2-} in soil solution demonstrated that 32-61% of the SO_4^{2-} leaving the catchment had interacted with organic S in the soil (Gélineau et al., 1989).

Plastic Lake (PC1) Watershed in Ontario had mean annual precipitation (992 mm yr^{-1}) that was 223 mm lower than the average of all watershed sites. The S precipitation input ($7.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was higher by $1.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ than the average for all sites. Dry deposition values (Equation 2: $1.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $3.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were higher by 0.5 and $1.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ respectively than the average for all watersheds. Using these dry deposition estimates, the watershed S discrepancies would be either $-2.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-13.8 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or $-0.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-3.9 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$), respectively. Previous work at PC1 has recognized these

discrepancies (e.g., Eimers and Dillon 2002). Sulfate export from PC1 is strongly influenced by the presence of a large (2.2 ha) conifer-*Sphagnum* swamp located directly upstream of the catchment outflow (e.g., LaZerte 1993). As a consequence of its location, more than 80% of the runoff draining from the upland part of PC1 passes through the wetland before discharging to Plastic Lake and therefore processes occurring in the wetland have a strong impact on stream chemistry. Wetland hydrology is particularly important for S cycling in this wetland-dominated catchment, and the S budget for the wetland (and the entire PC1 catchment) is strongly negative (net export) following periods of drought, when wetland water tables decline for extended periods allowing reoxidation of reduced S compounds (LaZerte, 1993; Eimers et al., 2007; Aherne et al., 2008). In contrast, during years with wet summers the S budgets for the wetland and the catchment as a whole are positive (Eimers et al., 2007). Isotopic analyses have shown that changes in SO_4^{2-} concentration in the wetland outflow and switches between net retention and net export are associated with microbial redox processes; there is no apparent weathering source of S in PC1 (Eimers et al., 2004ab).

Lake Clair Watershed in Quebec had mean annual precipitation (1286 mm yr⁻¹) that was higher by 71 mm than the average of all watershed sites. The S precipitation input (8.0 kg S ha⁻¹ yr⁻¹) was the third highest of all 15 watersheds and 1.5 kg S ha⁻¹ yr⁻¹ higher than the average value. This relatively high S in precipitation may be a reflection of some local point sources of S emission as discussed previously for area in close proximity to this site. Dry deposition values (Equation 2: 0.7 kg S ha⁻¹ yr⁻¹; Equation 3: 1.8 kg S ha⁻¹ yr⁻¹) were lower by 0.7 and 0.9 kg S ha⁻¹ yr⁻¹, respectively, than the average for all watersheds. Using these deposition estimates, the

watershed S discrepancies would be either $-4.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-13.4 \text{ } \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or $-3.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-9.9 \text{ } \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$), respectively. The pool of S in soils averaged 1455 kg ha^{-1} of which 1271 kg ha^{-1} (87%) was organic S. The remaining inorganic SO_4^{2-} (184 kg ha^{-1}) was mainly in the B horizons where adsorbed SO_4^{2-} represented 87% of inorganic SO_4^{2-} (Houle, unpublished data). Between 1988 and 1994, net SO_4^{2-} export occurred ($4.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$). These S losses were attributed to SO_4^{2-} desorption and/or organic S mineralization (Houle et al., 1997).

HBEF-W6 in the White Mountains of New Hampshire had mean annual precipitation (1410 mm yr^{-1}) for the study period that was higher than the average of all 15 watershed sites. The wet only input ($8.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was higher by $1.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ than the average of all sites. Dry deposition values (Equation 2: $1.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $2.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were substantially higher than the average for all watersheds (Equation 2: $1.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $2.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$). These dry deposition estimates are very similar to those of Cone Pond due to proximity of these two watersheds (Figure 3). These are consistent with previous estimates of S dry deposition at Hubbard Brook Watershed 6, made using multiple methods, which have ranged from 1.8 to $3.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ (Lovett et al., 1992, 1997). Using the dry deposition estimates from equations 2 and 3 in the current study, the watershed S discrepancies would be either $-3.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-12.1 \text{ } \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or $-2.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($7.4 \text{ } \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$), respectively. There has been considerable effort associated with the evaluation of S budgets at the Hubbard Brook Experimental Forest since 1964 including detailed evaluation of all components of the S budget and the effects of forest disturbance (e.g., Likens and Bormann, 1995; Likens et al., 2002). This

previous work has also suggested that there is a discrepancy in the net hydrologic S budgets (precipitation inputs minus streamwater outputs) for the various watersheds of the Hubbard Brook Experimental Forest including W6. The use of isotopic analyses ($\delta^{34}\text{S}$) of SO_4^{2-} including measurements over an extended period (1967-1994) using archived samples has suggested that the discrepancy is likely due to the mineralization of a small fraction of the large organic S pool (Alewell et al., 1999). The relative contributions of deposition, S mineral weathering, SO_4^{2-} desorption and organic S mineralization have also been evaluated by application of the PnET-BGC model which was modified to include evaluations of $\delta^{34}\text{S}$ (Gbondo-Tugbawa et al., 2002). These simulations also suggested the importance of the mineralization of the organic S pool in the soil as the major contributor to the discrepancy in the net hydrologic S budget (Gbondo-Tugbawa et al., 2002). Although S concentration is relatively high in some of the bedrock at HBEF, there is no evidence that weathering is a substantial S source (Likens et al., 2002; Bailey et al., 2004).

Biscuit Brook Watershed in the Catskill Mountains of New York had the highest precipitation amount (1525 mm yr^{-1}) and highest amounts of wet ($9.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) and dry deposition (Equation 2: $3.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $6.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) of all sites compared during the study period. Regardless of which values were used to estimate total wet plus dry atmospheric input there was substantial discrepancy (-3.7 to $-1.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, -11.5 and $-3.3 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$, respectively) in the watershed S balance. These results indicate a substantial net watershed loss of S and differ from an earlier study at Biscuit Brook in which S inputs were estimated to approximately balance outputs when dry S deposition was assumed to equal 33% of wet S

deposition (Stoddard and Murdoch, 1991). This earlier study was only for two years and used results from a period (1984-1985) with higher rates of sulfur deposition than for the average for the entire period (1985-2002) of the current study. This early work also assumed no mineral S source in the bedrock underlying Biscuit Brook, although pyrite had been recently identified nearby. Since stream data collection began in 1983 at Biscuit Brook, several studies have confirmed persistent trends of decreasing stream SO_4^{2-} concentrations as well as decreasing concentrations and fluxes of atmospheric S at the nearby NADP/NTN site (Murdoch and Stoddard, 1993; Burns et al., 2006; Murdoch and Shanley, 2006).

CATEGORY IV

All four of the sites in Category IV are in Canada and relatively remote from major sources of anthropogenic S deposition (Figure 3).

Turkey Lakes Watersheds in Ontario had mean annual precipitation (1230 mm yr^{-1}) that was similar to the average of all the study sites. For Turkey Lakes the discharge measurements were an average of 13 watersheds (31-35, 37-39, 42, 46-47, 49-50) with an annual average S export of $9.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ and a range of 7.5 to $11.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$. There are no obvious catchment characteristics, such as proportion of wetlands or relative elevation, which explain this variation. Schiff et al. (2005) showed that catchments with significant wetlands have important episodes of high stream SO_4^{2-} following summer droughts and the source of the S is from oxidation of reduced S in the upper layers of peat in the wetlands. The S precipitation input ($6.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was slightly higher by $0.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ than the average for all sites. Dry deposition values

(Equation 2: $1.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $3.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were slightly higher than the overall watershed averages. Using these dry deposition estimates, the watershed S discrepancies would be either $-1.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-6.0 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or $+0.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($2.6 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$), respectively. Hence for this watershed with relatively low atmospheric sulfur inputs differences in the estimates of dry deposition may result in the watershed showing small net SO_4^{2-} loss or retention. Some of the decrease in stream SO_4^{2-} over the study period is a result of concomitant decreases in precipitation concentrations (Beall et al., 2001). Some of this decrease may also be due to losses of exchangeable SO_4^{2-} from upper soils layers (Morrison et al., 1992; Morrison and Foster 2001). A comparison between S fluxes at Turkey Lakes and the Arbutus watersheds found that the latter site had lower atmospheric S inputs and lower SO_4^{2-} leaching rates although Turkey Lakes has a larger soil S pool (Mitchell et al., 1992).

Mersey Watershed in Kejimikujik National Park of Nova Scotia had mean annual precipitation (1331 mm yr^{-1}) that was higher than the average of all watershed sites. The S precipitation input ($4.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was lower by $1.7 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ than the average of all sites. Dry deposition values (Equation 2: $0.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $1.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were also lower than the average for all watersheds. Using these dry deposition estimates, the watershed S discrepancies would be either $-1.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-4.0 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or $-0.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($-0.4 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) respectively.

Lake Tirassee Watershed in Quebec, the most remote and northerly site, had the lowest annual precipitation (800 mm yr^{-1}) of all sites and also had the lowest S precipitation input (2.8 kg S ha^{-1}

yr⁻¹). Dry deposition values (Equation 2: 0.6 kg S ha⁻¹ yr⁻¹; Equation 3: 0.7 kg S ha⁻¹ yr⁻¹) were the lowest of the 15 watershed sites. Using these dry deposition estimates, the watershed S discrepancies would be either (Equation 2) -0.6 kg S ha⁻¹ yr⁻¹ (-3.1 μmol SO₄²⁻ L⁻¹) or (Equation 3) +0.3 kg S ha⁻¹ yr⁻¹ (2.1 μmol SO₄²⁻ L⁻¹), respectively. The lack of a decrease in SO₄²⁻ precipitation concentration during the 1997-2004 period contrasts with many other sites in the northeastern USA and southeastern Canada (Duchesne and Houle, 2006). This could be due to the relatively short data period (8 years) and also to the different periods of time that are compared and/or the remoteness of this site from S emission sources. The absence of an atmospheric trend at the Tirasse watershed during the relative short period of 1997-2004 fits well with reports of relatively similar SO₄²⁻ concentrations in wet precipitation since 1995 in both the US and Canada (Butler et al., 2001; Likens et al., 2001; Houle et al., 2004). Watershed S discrepancies of 0.9 kg ha⁻¹ yr⁻¹ have been previously documented using throughfall S deposition, plus the contribution of dissolved organic sulfur (DOS) in incoming precipitation as a surrogate of total S deposition during the 1997-2003 period. These studies have also suggested that mineralization of soil organic S was the likely source of the excess S (Duchesne and Houle, 2006).

Moosepit Watershed also in Kejimikujik National Park of Nova Scotia used the same mean annual precipitation (1331 mm yr⁻¹) measurements as Mersey Watershed due to their close proximity. The S precipitation measurement (4.8 kg S ha⁻¹ yr⁻¹) and dry deposition estimates were also identical to Mersey Watershed. Using our dry deposition equations, the watershed S discrepancies would be either -1.0 kg S ha⁻¹ yr⁻¹ (-2.8 μmol SO₄²⁻ L⁻¹) or 0.1 kg S ha⁻¹ yr⁻¹ (0.8

$\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$), respectively and hence using the higher values (Equation 3) results in this watershed being a net sink for atmospheric S inputs. These results provide a different estimate over that of Yanni et al. (2000) who could only ascribe a discrepancy between measured wet CAPMoN deposition and export to fog deposition.

CATEGORY V

Hermine Watershed in Quebec had mean annual precipitation (1162 mm yr^{-1}) that was lower by 62 mm than the average of all watershed sites. The mean annual discharge (441 mm yr^{-1}) of the Hermine was the lowest among the catchments studied. It follows that the Hermine has a discharge ratio (discharge/precipitation) of about 38%, a low value for forested watersheds of Northeastern North America. The S precipitation input ($6.8 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) was slightly higher by $0.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ than average of all sites and similar to annual S output in streamwater. Dry deposition values (Equation 2: $1.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$; Equation 3: $2.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$) were lower by 0.4 and $0.6 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ respectively, than the average for all watersheds. Using these dry deposition estimates, the watershed S discrepancies would be either (Equation 2) $+0.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($14.4 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$) or (Equation 3) $+1.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ($22.5 \mu\text{mol SO}_4^{2-} \text{ L}^{-1}$). Along with the Turkey Lakes and Lake Tirassee catchments, Hermine is the only watershed apparently retaining S on a mean annual basis. The estimated discrepancies of $+0.4$ to $1.5 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ suggest that 5 to 22% of total annual S inputs are retained in the catchment, a high value for a non-aggrading forested ecosystems. Hermine retained S (1.9 to $3.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ with eq. 3) during four of the five years of the data set. In all cases, these were years much dryer than average with less than 1150 mm precipitation and high summer temperatures that caused streamflow to cease for

prolonged periods during the growing season. Sulfur was lost (-1.2 to -4.2 kg S ha⁻¹ yr⁻¹ with eq. 3) from the watershed when the Hermine experienced cooler and much wetter conditions. Such dry years were substantial within the five-year record used for this watershed. Previous work showed the capacity of the podzolic B horizons of the Hermine soils to retain SO₄²⁻ up to 1 to 3 mmol SO₄²⁻ kg⁻¹ soil (Courchesne and Hendershot, 1989).

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