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# Comparisons of watershed sulfur budgets in southeast Canada and northeast US: new approaches and implications

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**Abstract** Most of eastern North America receives elevated levels of atmospheric deposition of sulfur (S) that result from anthropogenic $SO_2$ 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 Tirasse, QC; Mersey, NS; Moosepit, NS) and

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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 $SO_4^{2-}$ 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 the US (CASTNET) and the Canadian (CAPMoN) dry deposition networks to develop a formulation that predicted $SO_2$ concentrations as a function of $SO_2$ emissions, latitude and longitude. The $SO_2$ 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 $SO_2$ 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 $SO_2$ concentrations and S deposition for the region that is 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 $SO_4^{2-}$ 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 $SO_4^{2-}$ 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 $SO_4^{2-}$, 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

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1–6 kg S $ha^{-1}$ $year^{-1}$ 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.

**Keywords** Watersheds · Sulfur budgets · Atmospheric deposition models · Acidic deposition · Recovery · Northeast US · Southeast Canada

## Introduction

Anthropogenic emissions of sulfur dioxide ($SO_2$) 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 (Fig. 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 $SO_2$ emissions. Similarly, implementation of the Eastern Canada Acid Rain Program reduced Canadian emissions such that total Canada-US $SO_2$ 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 $SO_2$ and $SO_4^{2-}$ aerosols; Baumgardner et al. 2002). These decreases in atmospheric S inputs have also resulted in decreases in $SO_4^{2-}$ concentrations in surface waters with notable decreases across southeastern Canada (Clair et al. 1995; Jeffries et al. 2003a, b; 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).

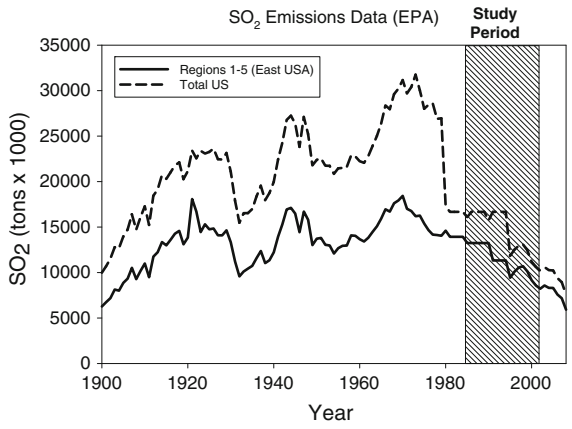


**Fig. 1** $SO_2$ emissions for entire United States and Regions 1–5 (eastern U.S.) from 1900 to 2008. Source of information is provided in the text

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, 1998; 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).

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## 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 $SO_4^{2-}$ (Fig. 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.

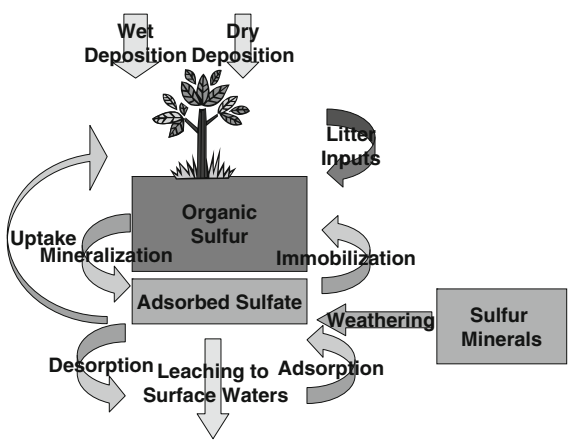


**Fig. 2** Major sulfur pools and fluxes in a forested watershed

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. 1992a, b; Jeffries et al. 2003a, b; 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. 1992a). 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. 1992a, 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. 1999; 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) (Moran et al. 2008; 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 Carignan 1992; Mitchell et al. 1992a, b). 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 $\delta^{34}S$ and $\delta^{18}O$) 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 (Fig. 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 Fig. 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,

**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 | *Acer rubrum*, *Fagus grandifolia*, *Acer saccharum*, *Betula Alleghaniensis* | 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 | *Picea rubens*, *Abies balsamea*, *Tsuga canadensis*, *F. grandifolia*, *A. saccharum* | 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 | *A. saccharum*, *F. grandifolia*, *B. allegheniensis*, *A. balsamea*, *P. rubea* | 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 | *F. grandifolia*, *A. saccharum*, *T. canadensis* | Mitchell et al. (2001b, 2006) |
| Mersey Watershed | Mersey | Kejimkujik National Park, Nova Scotia, Canada | 44.42 | −65.23 | 29,500 | Uplands are shallow podsols with gleysols and fens and peat bogs | *P. glauca mariana*, *A. balsamea*, *Pinus strobus*, *T. canadensis*, *A. saccharum*, *B. papyrifera*, *F. grandifolia* | Yanni et al. (2000) |
| Moosepit Watershed | Moosepit | Kejimkujik 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 | *P. glauca mariana*, *A. balsamea*, *P. strobus*, *T. canadensis*, *A. saccharum*, *B. papyrifera*, *Fagus grandifolia* | Yanni et al. (2000) |
| Sleepers River, Watershed 9 | Sleepers | Vermont, USA | 44.48 | −72.17 | 40.5 | Typic Dydtrudepts (40%), Humic Dydtrudepts (20%), Aquic Dystric Eutrudepts (20%), Typic Humaquepts (20%) | *A. saccharum*, *B. alleghaniensis*, *Fraxinus americana* | Shanley et al. (2005, 2008) |
| Bear Brook (East) | Bear | Maine, USA | 44.87 | −68.1 | 10.3 | Typic Haplorthods | *F. grandifolia*, *A. rubrum* L., *A. saccharum*, *B. alleghaniensis*, *P. rubens* | David et al. (1990), Stam et al. (1992), Norton and Fernandez (1999) |

**Table 1** continued

| Watershed | Short name | Location | Latitude | Longitude | Size (ha) | Soil type | Dominant vegetation | Selected references |
|---|---|---|---|---|---|---|---|---|
| Plastic Lake (PC1) | Plastic | Ontario, Canada | 45.18 | −78.83 | 23.3 | Acidic podsols in uplands, organic soils and gleysols in depressions and wetlands | *Pinus strobus*, *Tsuga canadensis*, *Quercus rubra*, *Thuja occidentalis*, *Picea mariana* | Dillon and LaZerte (1992), LaZerte (1993) |
| Harp Lake (HP3A) | Harp | Ontario, Canada | 45.38 | −79.12 | 3.7 | Acidic podsols in uplands, organic soils and gleysols in depressions and wetlands | *Acer saccharum*, *Acer rubrum*, *Populus grandidenta*, *Fagus grandifolia* | 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 | *A. saccharum*, *F. grandifolia*, *B. alleghaniensis* | Biron et al. (1999), Bélanger et al. (2002), Courchesne et al. (2005) |
| Lake Clair | Clair | Centre récrétotouristique de Duchesnay, Quebec, Canada | 46.95 | −71.67 | 226 | Entic Haplorthod or Ferro-Humic Podzol | *Acer saccharum*, *Fagus grandifolia*, *Betula alleghaniensis* | 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 | *Abies balsamea*, *Picea glauca*, *Betula papyrifera* | 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 | 3–115 | Uplands: Haplohumods and Haplorthods; Wetland: Haplohemists | *A. saccharum* (90%), *B. alleghaniensis*, *P. strobus*, *P. glauca* | 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 | *P. mariana*, *P. banksiana* | Duchesne and Houle (2006) |

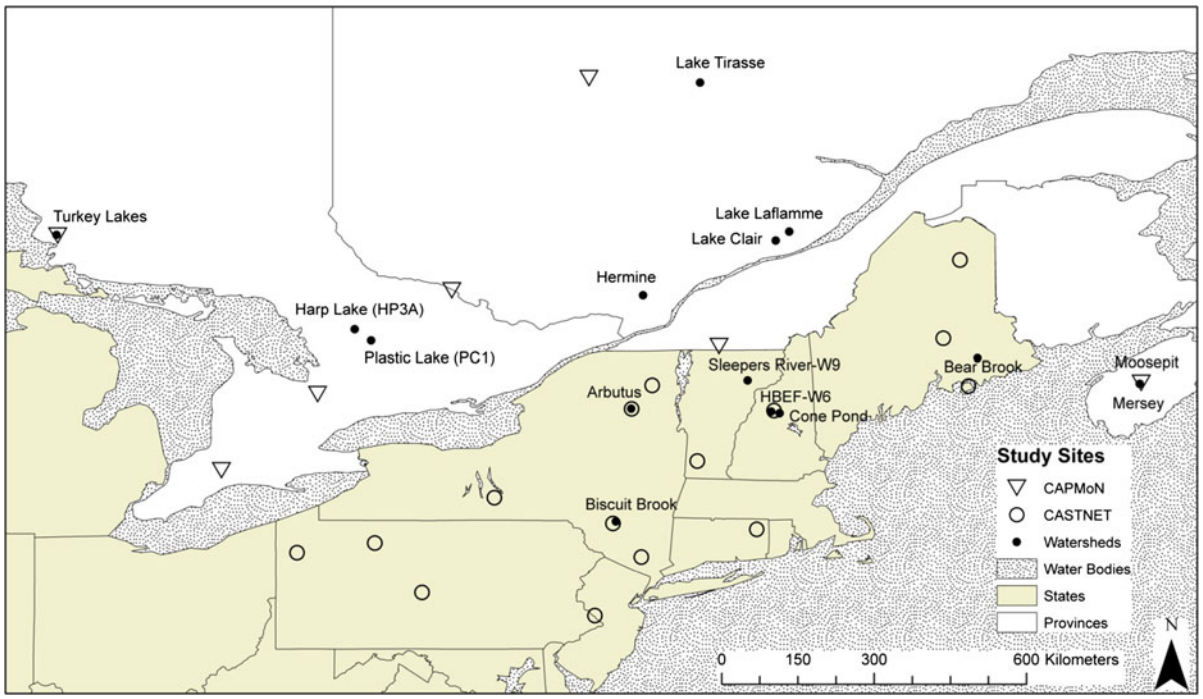


**Fig. 3** Location of watersheds in the northeastern U.S. and southeastern Canada with information on sulfur budgets and location of CASTNET and CAPMoN sites used in developing Eq. 1

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 $SO_2$ concentration data from dry deposition monitoring networks in the northeastern US (CASTNET) and southeastern Canada (CAPMoN) along with annual eastern US $SO_2$ emissions data to develop an empirical relationship. This relationship was then used to determine the spatial and temporal patterns of $SO_2$ concentrations in the air at the watershed locations. To match the geographical area of the watersheds we were studying, we used $SO_2$ 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 (Fig. 3). The estimates of annual $SO_2$ emissions were derived from the US EPA estimates of the Acid Rain Program sources located in eastern US (EPA Regions

**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 min | Weekly + Events |
| Cone Pond | 1985–2002 | Bulk | Continuous | Weekly+ |
| HBEF | 1985–2002 | Bulk | Continuous | Weekly |
| Arbutus | 1985–2002 | Wet only (NADP) | 15 min | 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 min | Weekly |
| Plastic Lake | 1985–1997 | Bulk | 10 min | Weekly + Events |
| Harp Lake | 1985–1997 | Bulk | 10 min | Weekly + Events |
| Hermine | 1995–1997, 2001–2002 | Bulk | Daily | Daily |
| Lake Clair | 1985–2002 | Bulk | Read every 5 s/1 h average recorded | Weekly |
| Lake Laflamme | 1985–1996, 1999–2002 | Wet Only | Read every 5 s/1 h average recorded | Weekly |
| Turkey Lakes[a] | 1985–2002 | Wet only | Continuous | Daily during peak melt, bi-weekly remainder of year |
| Lake Tirasse | 1997–2002 | Bulk | Read every 5 s/1 h average recorded | Weekly |

[a] Mean values of Discharge for watersheds 31, 32, 33, 34, 35, 37, 38, 39, 42, 46, 47, 49, 50

1 through 5): http://camddataandmaps.epa.gov/gdm/index.cfm?fuseaction=emissions.wizard. Previous analyses have indicated that the Canadian $SO_2$ emissions constitute a small ($\sim$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 $SO_2$ emissions declined substantially for the period of our study (1985-2002) (Fig. 1), illustrating the importance of including a temporal component to the dry deposition calculations. Note that $SO_2$ 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 $SO_2$ concentration and latitude, longitude and annual eastern US $SO_2$ emissions were tested and we found that an asymptotic exponential function (Eq. 1, Fig. 4) explained 88% of the variation in predicted versus observed $SO_2$ concentrations with little bias (slope of 1.0).

$$SO_{2ave} = 0.9 + \exp\left(7.867 - 0.4633 * \text{lat} + 0.1494 * \text{long} + 1.863e - 7 * \text{toteast}SO_2\right) \quad (1)$$

where $SO_{2ave}$ is the annual average $SO_2$ concentration ($\mu g\ m^{-3}$) for each site and year, lat is ° north latitude, long is ° west longitude, and toteast$SO_2$ is the total emissions (tons per year) of $SO_2$ from the eastern US for the year.

Using Eq. 1, the average annual $SO_2$ concentrations for each site were calculated. The mean and range of $SO_2$ concentrations across the years of the study are shown in Fig. 5 with sites ranked by latitude from south to north. For all sites the mean $SO_2$ concentration was 1.2 $\mu g\ S\text{-}SO_2\ m^{-3}$, the maximum concentration was at Biscuit Brook (3.2 $\mu g\ S\text{-}SO_2\ m^{-3}$) and the minimum concentration at Lake Tirasse (0.5 $\mu g\ S\text{-}SO_2\ m^{-3}$)

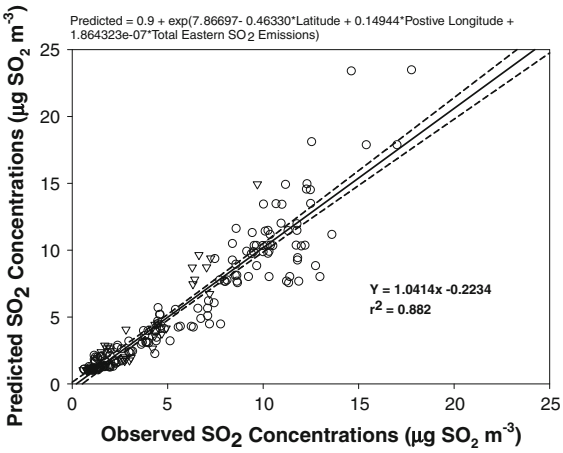


**Fig. 4** *Solid line* is regression equation of observed versus predicted annual $SO_2$ concentrations as a function of latitude, longitude and $SO_2$ emissions from the eastern United States for CASTNET and CAPMoN sites. *Dashed lines* are 95% confidence limits. Sites used in these calculation are shown in Fig. 3

(Fig. 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. 2008), which were run using the full US and Canada emissions inventories, with the values predicted for each watershed from Eq. 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 $SO_2$ 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 Eq. 1 are quite similar to those predicted by the two regional air quality models for most sites. If we exclude the Lake Clair $SO_2$ estimate for AURAMS, there are strong and highly significant correlations ($r = 0.731$ to 0.886, $p < 0.01$) among $SO_2$ concentration estimates for each site using Eq. 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 $SO_2$ concentration and modeled total S dry deposition ($SO_2$ plus $SO_4$ 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

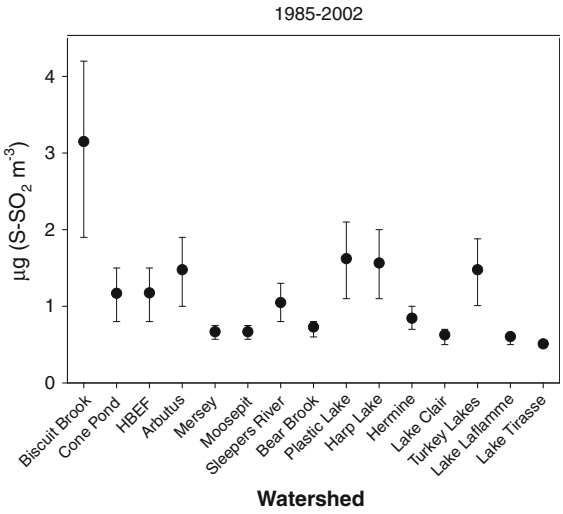


**Fig. 5** Range and mean values of calculated $SO_2$ concentrations for the period from 1985 to 2002 using formulation based upon latitude, longitude and eastern U.S. $SO_2$ emissions for the study sites (see text for details)

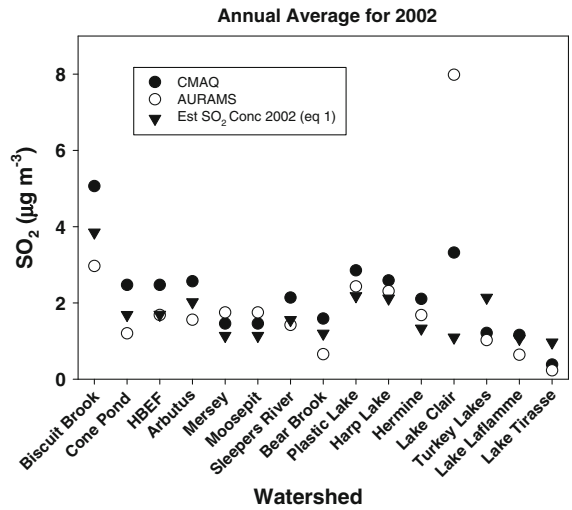


**Fig. 6** Predicted $SO_2$ concentrations for study region for CMAQ model, AURAMS model, and Eq. 1 for year 2002

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 $SO_2$ and $SO_4^{2-}$ were almost identical for the CASTNET and CAPMoN measurements, but the CAPMoN deposition estimates for $SO_2$ and $SO_4^{2-}$ 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 $SO_2$ concentration and total S dry deposition (Fig. 7). The two equations are:

CASTNET Equation:

$$\mathrm{kg\,S\,ha^{-1}\,year^{-1}} = \mathrm{SO_2\,(\mu g\,S\,m^{-3})} * 1.169 + 0.00572 \qquad r^2 = 0.901 \qquad (2)$$

where $SO_2$ values are average yearly concentrations for each CASTNET site.

CAPMoN Equation:

$$\mathrm{kg\,S\,ha^{-1}\,year^{-1}} = \mathrm{SO_2\,(\mu g\,S\,m^{-3})} * 1.696 + 0.694 \qquad r^2 = 0.928 \qquad (3)$$

where $SO_2$ 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 Eqs. 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 Eqs. 2 and 3 alone (Fig. 8). As noted previously there is a notable difference for the Lake Clair watershed where a local $SO_2$ 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 ($r = 0.607$–$0.880$, $p \leq 0.02$) between the dry S deposition estimates among sites for year 2002 using AURAMS, CMAQ, Eqs. 2 and 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 Eqs. 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.

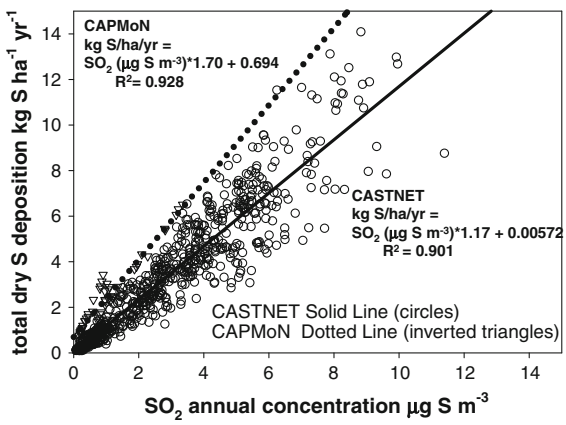


**Fig. 7** Calculated relationships between annual $SO_2$ concentrations and total dry deposition of S using data for CASTNET (Equation 2) and CAPMoN (Equation 3) sites

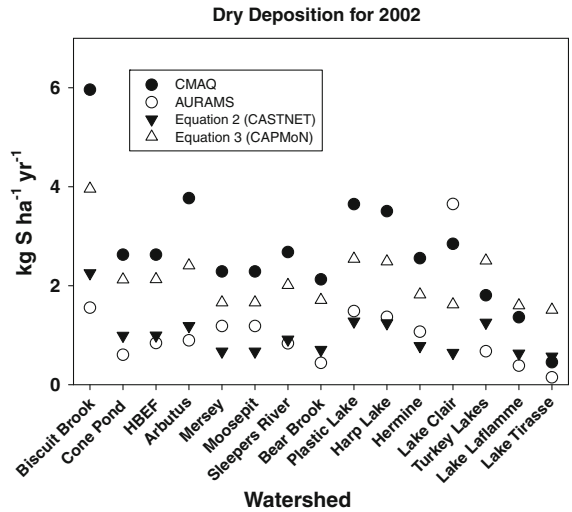


**Fig. 8** Predicted S dry deposition for study region for CMAQ model, AURAMS model, Equation 2 (CASTNET data) and Equation 3 (CAPMoN data) for year 2002

## 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 Tirasse and the maximum (1800 mm) at Biscuit Brook (Fig. 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 Tirasse and a maximum (721 mm) at Hermine. The mean annual precipitation, discharge and evapotranspiration values for each watershed are provided in Fig. 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 kg S $ha^{-1}$ $year^{-1}$ with a minimum at Lake Tirasse (0.6 kg S $ha^{-1}$ $year^{-1}$) and a maximum at Biscuit Brook (3.7 kg S $ha^{-1}$ $year^{-1}$). The use of CAPMoN-based Equation 3 resulted in substantially higher mean dry deposition estimates of 2.7 kg S $ha^{-1}$ $year^{-1}$ with a minimum at Lake Tirasse (1.6 kg S $ha^{-1}$ $year^{-1}$) and a maximum at Biscuit Brook (6.0 kg S $ha^{-1}$ $year^{-1}$). Average $SO_4^{2-}$ discharge among watersheds was 11.3 kg S $ha^{-1}$ $year^{-1}$ with a large range among watersheds from 4.0 kg S $ha^{-1}$ $year^{-1}$ (Lake Tirasse) to 17.7 kg S $ha^{-1}$ $year^{-1}$ (Sleepers River) (Fig. 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 (Fig. 10). The use of Eq. 2 resulted in a mean discrepancy of −3.5 kg S $ha^{-1}$ $year^{-1}$ with the smallest (+0.4 kg S $ha^{-1}$ $year^{-1}$) at Hermine, which was the only watershed to show net S retention using this estimate of total atmospheric deposition, and a largest (−10.0 kg S $ha^{-1}$ $year^{-1}$) at Sleepers River. Using this latter estimate, four watersheds out of the 15 sites showed net S retention (Hermine: +1.5 kg S $ha^{-1}$ $year^{-1}$; Lake Tirasse: +0.3 kg S $ha^{-1}$ $year^{-1}$; Turkey Lakes:

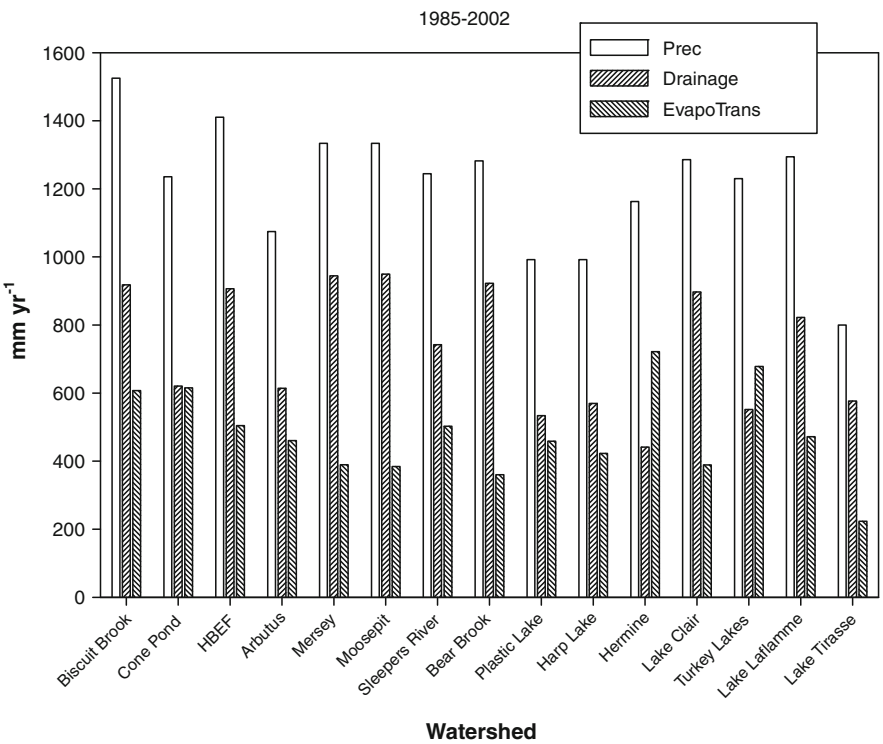


**Fig. 9** Mean annual precipitation, discharge values and calculated evapotranspiration (precipitation–discharge) for each watershed for the period from 1985 through 2002. For details on data utilized see Table 1

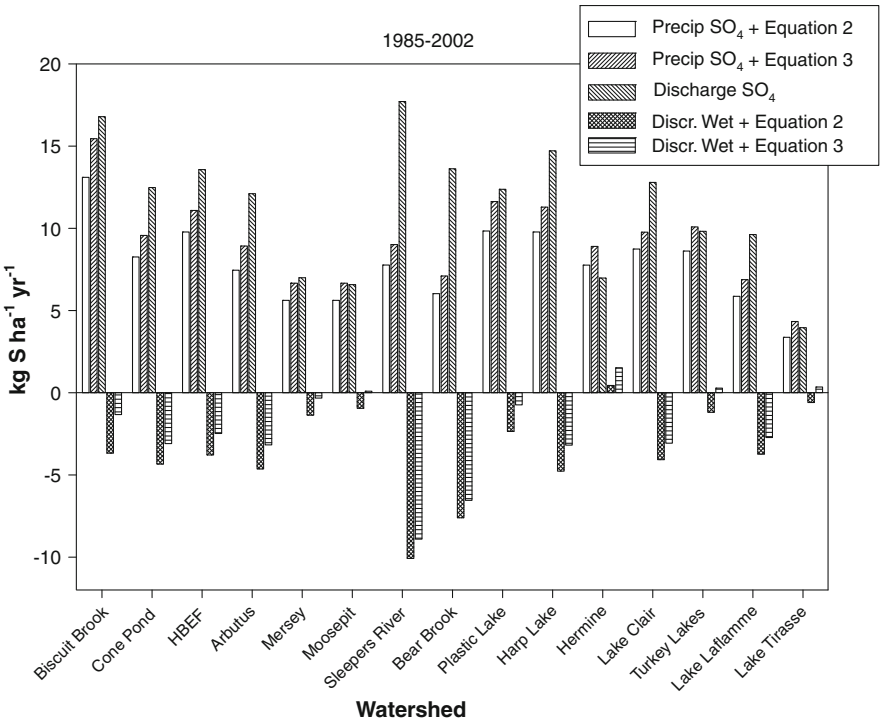


**Fig. 10** Annual fluxes of total atmospheric sulfur deposition (precipitation combined with estimates of dry deposition based upon Eqs. 2 or 3, see text for details) with discrepancy calculated by subtracting sulfur in discharge from the estimates of total atmospheric sulfur deposition

+0.3 kg S ha$^{-1}$ year$^{-1}$ Moosepit: +0.1 kg S ha$^{-1}$ year$^{-1}$). The use of Eq. 3 resulted in a lower mean discrepancy of −2.2 kg S ha$^{-1}$ year$^{-1}$ with the smallest difference (−0.2 and +0.2 kg S ha$^{-1}$ year$^{-1}$) at (Mersey and Moosepit, respectively) and largest difference (−10.1 kg S ha$^{-1}$ year$^{-1}$) 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 μmol $SO_4^{2-}$ l$^{-1}$. Using appropriate conversions from mass to molar values and dividing the annual $SO_4^{2-}$ flux value of precipitation or discharge (kg S-$SO_4^{2-}$ ha$^{-1}$ year$^{-1}$) by water flux (mm year$^{-1}$), we converted these values to μmol $SO_4^{2-}$ 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

**Table 3** Temporal changes (annual values) for precipitation and discharge from 1985 through 2002 (significant values $p \leq 0.05$ are given in **bold**)

| Watershed | Precip. flux (kg S $ha^{-1}$ $year^{-1}$) | *p* value | Precip. conc. (μmol $SO_4^{2-}$ $l^{-1}$ $year^{-1}$) | *p* value | Discharge conc. (μmol $SO_4^{2-}$ $l^{-1}$ $year^{-1}$) | *p* value |
|---|---|---|---|---|---|---|
| Biscuit Brook | **−0.28** | **0.0003** | **−0.61** | **0.0001** | **−1.29** | **<0.0001** |
| 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** | **<0.0001** |
| Arbutus | **−0.18** | **0.0002** | **−0.58** | **<0.0001** | **−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** | **<0.0001** |
| Lake Laflamme | **−0.12** | **0.0347** | −0.21 | 0.0771 | **−1.18** | **<0.0001** |
| 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** |

$SO_4^{2-}$ budgets are provided for Hubbard Brook Experimental Forest Watershed 6 (Fig. 11) and Turkey Lakes (Fig. 12) along with their respective annual hydrological fluxes (Figs. 13, 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 kg S $ha^{-1}$ $year^{-1}$ were converted to mean annual, volume-weighted concentration values (μmol $SO_4^{2-}$ $l^{-1}$) 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 Fig. 15. Only Lake Laflamme showed a significant trend in concentration discrepancies over time (total deposition using Eq. 2: slope = 0.908 μmol $SO_4^{2-}$ $year^{-1}$, $p \leq 0.0001$; total deposition using Eq. 3: slope = 0.880 μmol $SO_4^{2-}$ $year^{-1}$, $p = 0.0001$) 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 (Fig. 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

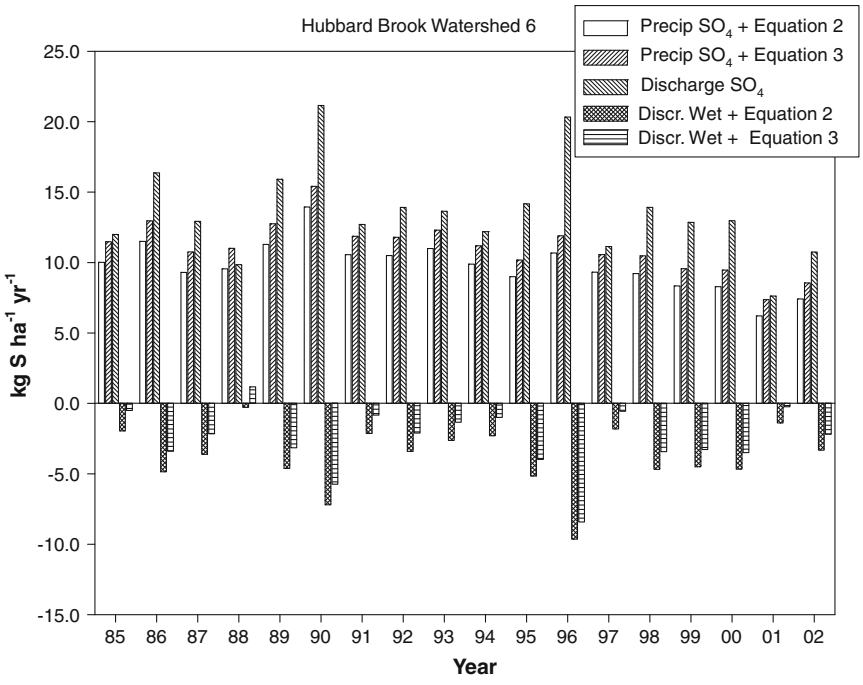


**Fig. 11** Annual sulfur budgets for Hubbard Brook Watershed 6: bulk precipitation + either Equation 2 or Equation 3 dry deposition estimates, discharge and discrepancy using Eq. 2 or Eq. 3 deposition estimates

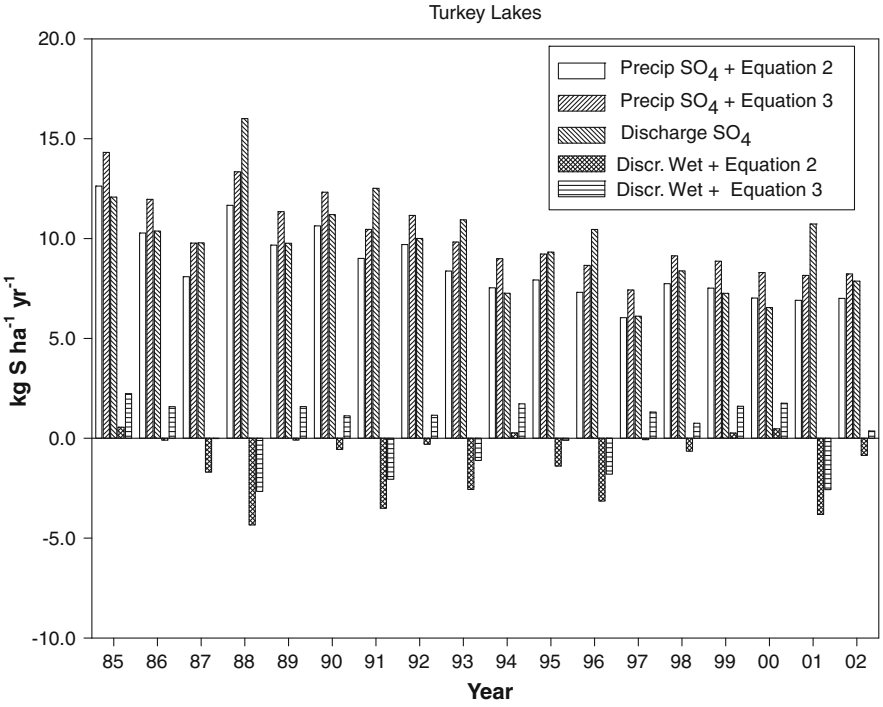


**Fig. 12** Annual sulfur budgets for Turkey Lakes watersheds: bulk precipitation + either Equation 2 or Equation 3 dry deposition estimates, discharge (average of watersheds as detailed in text) and discrepancy using either Eq. 2 or Eq. 3 deposition estimates

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. 2004a, c; Arbutus: Mitchell et al. 2006, 2008; Sleepers River: Mitchell

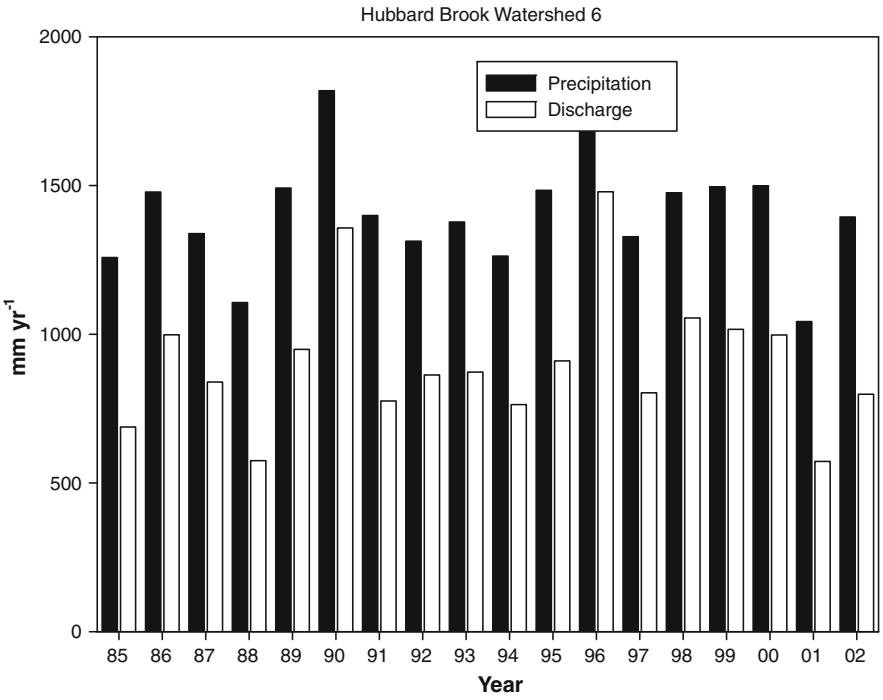


**Fig. 13** Annual hydrology (precipitation and discharge) for Hubbard Brook Watershed 6

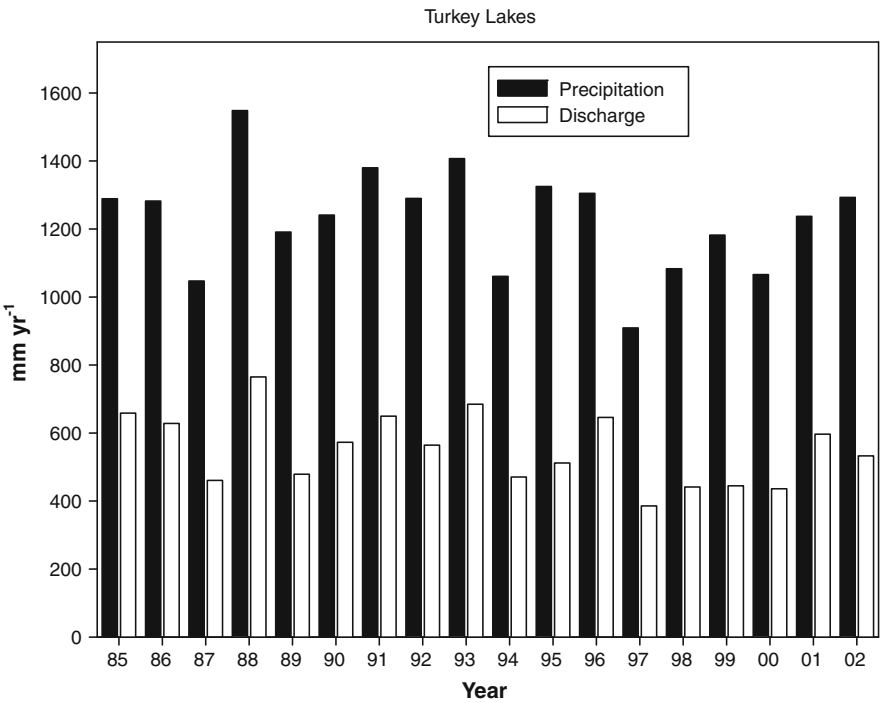


**Fig. 14** Annual hydrology (precipitation and discharge) for Turkey Lakes (discharge averaged for watersheds as detailed in text)

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.

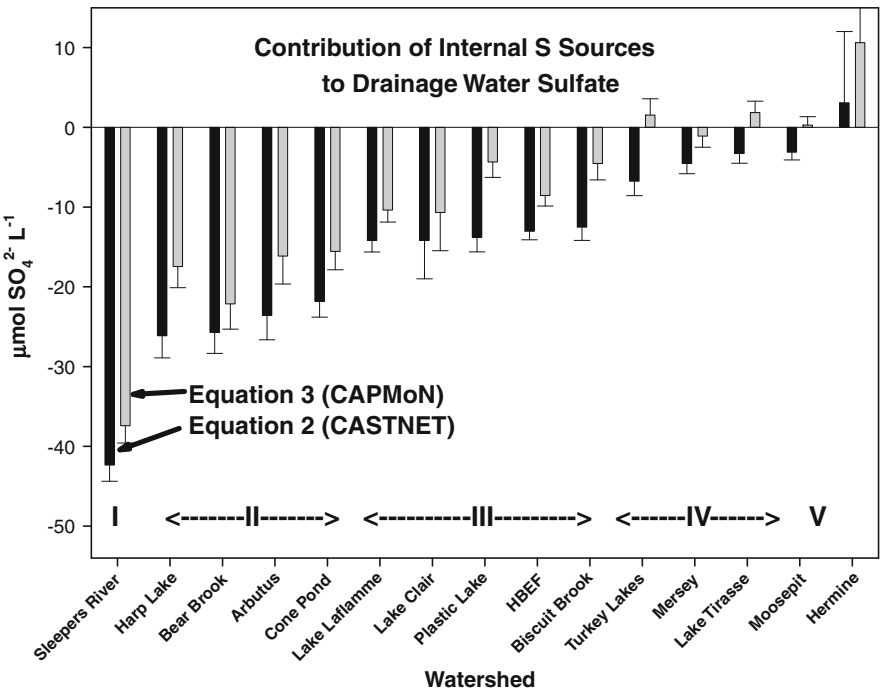


**Fig. 15** Classification of watersheds based upon the $SO_4^{2-}$ concentration contributed by internal sulfur sources. Error bars are 1 standard error. See text for details on rationale of classification

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 (Fig. 15). For more details on the S budgets and biogeochemistry of individual sites see Appendix I—Supplementary material.

*Category I*: Clearly, Sleepers River has the greatest discrepancy (−37 to −42 µmol $SO_4^{2-}$ $l^{-1}$) of all other sites by >13 µmol $SO_4^{2-}$ $l^{-1}$ 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 µmol $SO_4^{2-}$ $l^{-1}$ (using Eq. 2 estimates) or −14 to −23 µmol $SO_4^{2-}$ $l^{-1}$ (using Eq. 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 ($\delta^{34}$S-$SO_4^{2-}$) 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 ($\delta^{18}$O and $\delta^{34}$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 µmol

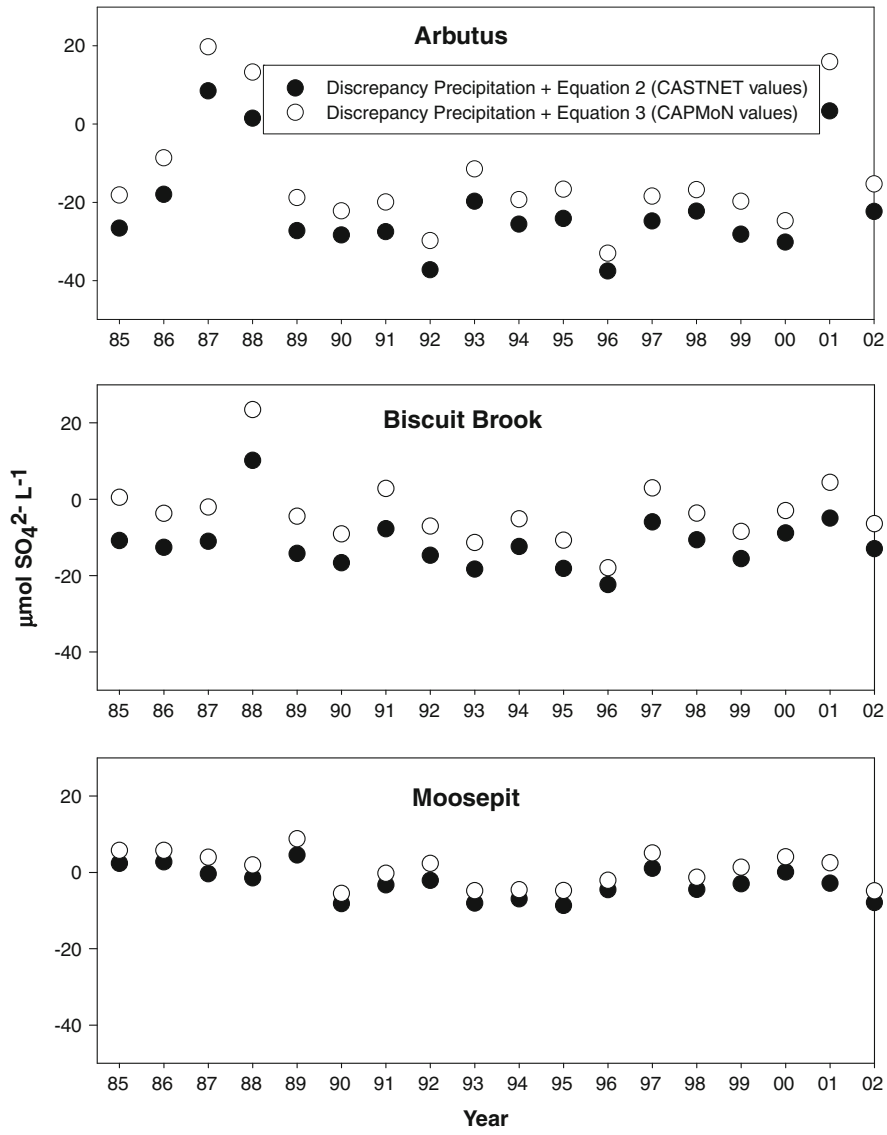


**Fig. 16** Mass balance annual discrepancy value in $SO_4^{2-}$ concentrations calculated from the differences in discharge–precipitation + dry deposition from Equation 2 (CASTNET values) (*closed circle*) and precipitation + dry deposition from Equation 3 (CAPMoN values) (*open circle*) for Arbutus, Biscuit Brook and Moosepit. See text for further details on the calculations

$SO_4^{2-}$ $l^{-1}$ (using Eq. 2 estimates) or −3 to −10 µmol $SO_4^{2-}$ $l^{-1}$ (using Eq. 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. 2004a, b). 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.,

**Table 4** Discrepancies calculated using μmol $SO_4^{2-}$ 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 | <0.0001 | −0.024 | <0.0001 |
| 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 |

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 ($\delta^{34}S$) 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 2 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 μmol $SO_4^{2-}$ $l^{-1}$). For all of these sites, except Mersey, the utilization of the higher dry deposition estimates using Eq. 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 (Fig. 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 kg $ha^{-1}$ $year^{-1}$ 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 μmol $SO_4^{2-}$ $l^{-1}$) 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 Tirasse catchments (using Eq. 3), Hermine is the only watershed apparently retaining S on a mean annual basis using Eqs. 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 kg S $ha^{-1}$ $year^{-1}$ with Eq. 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, $SO_2$ 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 $SO_4^{2-}$ 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 $SO_4^{2-}$ 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 $SO_4^{2-}$ discrepancy values (i.e., $-3$ to $-27$ μmol $SO_4^{2-}$ $l^{-1}$; Fig. 15; Categories II and III) and using the average annual discharge for the 15 sites (737 mm $year^{-1}$). 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 $ha^{-1}$ $year^{-1}$ in the annual $SO_4^{2-}$ export. Other studies have suggested that although there may be some contribution from the desorption of $SO_4^{2-}$ that accumulated during periods of higher S deposition, the $SO_4^{2-}$ adsorption capacities of the soils in this region are relatively small (Rochelle et al. 1987; Mitchell et al. 1992a, b; Houle and Carignan 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 (Alewell et al. 1999, 2000; Likens et al. 2002; Gélineau et al. 1989) and Europe (Novák 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 Eq. 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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