A BIOGEOCHEMICAL COMPARISON OF TWO WELL-BUFFERED CATCHMENTS WITH CONTRASTING HISTORIES OF ACID DEPOSITION

JAMES B. SHANLEY[1]*, PAVEL KRÁM[2], JAKUB HRUŠKA[2] and THOMAS D. BULLEN[3]

[1] *U.S. Geological Survey, P.O. Box 628, Montpelier, Vermont 05601, U.S.A.;* [2] *Czech Geological Survey, Klárov 3, CZ 118 21 Prague 1, Czech Republic;* [3] *U.S. Geological Survey, MS 420, 345 Middlefield Rd., Menlo Park, California 94025, U.S.A.*

(author for correspondence, e-mail: jshanley@usgs.gov, phone: (802) 828 4466, fax: (802) 828 4465)*

(Received 20 August 2002; accepted 10 April 2003)

Abstract. Much of the biogeochemical cycling research in catchments in the past 25 years has been driven by acid deposition research funding. This research has focused on vulnerable base-poor systems; catchments on alkaline lithologies have received little attention. In regions of high acid loadings, however, even well-buffered catchments are susceptible to forest decline and episodes of low alkalinity in streamwater. As part of a collaboration between the Czech and U.S. Geological Surveys, we compared biogeochemical patterns in two well-studied, well-buffered catchments: Pluhuv Bor in the western Czech Republic, which has received high loading of atmospheric acidity, and Sleepers River Research Watershed in Vermont, U.S.A., where acid loading has been considerably less. Despite differences in lithology, wetness, forest type, and glacial history, the catchments displayed similar patterns of solute concentrations and flow. At both catchments, base cation and alkalinity diluted with increasing flow, whereas nitrate and dissolved organic carbon increased with increasing flow. Sulfate diluted with increasing flow at Sleepers River, while at Pluhuv Bor the sulfate-flow relation shifted from positive to negative as atmospheric sulfur (S) loadings decreased and soil S pools were depleted during the 1990s. At high flow, alkalinity decreased to near 100 μeq L^{-1} at Pluhuv Bor compared to 400 μeq L^{-1} at Sleepers River. Despite the large amounts of S flushed from Pluhuv Bor soils, these alkalinity declines were caused solely by dilution, which was greater at Pluhuv Bor relative to Sleepers River due to greater contributions from shallow flow paths at high flow. Although the historical high S loading at Pluhuv Bor has caused soil acidification and possible forest damage, it has had little effect on the acid/base status of streamwater in this well-buffered catchment.

Keywords: acidification, alkalinity, base cations, buffering, catchments, Czech Republic, nitrate, sulfate, Vermont

1. Introduction

A rapid increase in coal burning in the present-day Czech Republic after World War II caused extremely high acid loadings (Kopáček *et al.*, 2001; Hruška *et al.*, 2002), which by the 1980s led to large areas of forest dieback and mortality. High-S emissions in close proximity to mountain ranges with little innate buffering capacity exacerbated the problem. In the U.S.A., damage has been more subtle, but over a much broader region. Forest decline and limited mortality have been linked to acid deposition in some areas (Driscoll *et al.*, 2001). As in the U.S.A., some areas of the Czech Republic have lithologies that are resistant to chemical weathering and have limited ability to buffer soils and waters.

In this paper, we compare the biogeochemistry of two well-buffered catchments. Sleepers River Research Watershed (Sleepers River) in the U.S.A. is buffered primarily by calcite within the phyllite bedrock. The Pluhuv Bor catchment (Pluhuv Bor) in the Czech Republic is buffered primarily by the weathering of antigorite in the serpentinite bedrock (Krám and Hruška, 1994). Present-day precipitation at both sites has a pH of 4.6. Pluhuv Bor is not in the area of the most serious forest damage, but it received much higher loadings of atmospheric acidity than Sleepers River during the last two decades. Our central question is how stream chemical patterns and trends and forest health may differ in these two well-buffered catchments as a result of their differing histories of atmospheric deposition.

Catchment biogeochemistry research has proliferated in the past few decades, largely due to funding for study of acid-deposition effects. This research has understandably focused on base-poor ecosystems, which are most susceptible to acidification and adverse ecological effects. Well-buffered sites, thought to be relatively immune from acidification, have received less study. The two well-buffered catchments discussed here are exceptions, having been the focus of intensive hydrologic and biogeochemical investigation for more than a decade.

Pluhuv Bor was established as a research site in 1991 by the Czech Geological Survey. It is the well-buffered catchment in a paired catchment study with the acidic Lysina catchment nearby (Krám and Hruška, 1994; Krám *et al.*, 1997; Hruška *et al.*, 2002). These catchments became part of the GEOMON network of 14 monitoring catchments in the Czech Republic (Novák *et al.*, 1996; Fottová and Skořepová, 1998). Sleepers River Research Watershed was established as a research site in 1957 by the Agricultural Research Service. In 1991, it was selected as one of five sites in the U.S. Geological Survey's Water, Energy, and Biogeochemical Budgets (WEBB) Program (Shanley and Chalmers, 1999; Shanley *et al.*, 2002a, b). At both sites, regular monitoring of water and solute fluxes in atmospheric deposition and streamflow has been ongoing for more than a decade. This paper is part of a collaboration between the U.S. and Czech Geological Surveys.

The objectives of this paper are (1) to compare trends in stream chemistry and solute fluxes in response to contrasting trends in atmospheric deposition at two similarly well-buffered catchments, (2) to compare biogeochemical processes and solute behavior at different flow regimes and to evaluate whether high loadings of atmospheric acidity may compromise the buffering capacity of well-buffered catchments, and (3) to compare forest health at the two catchments.

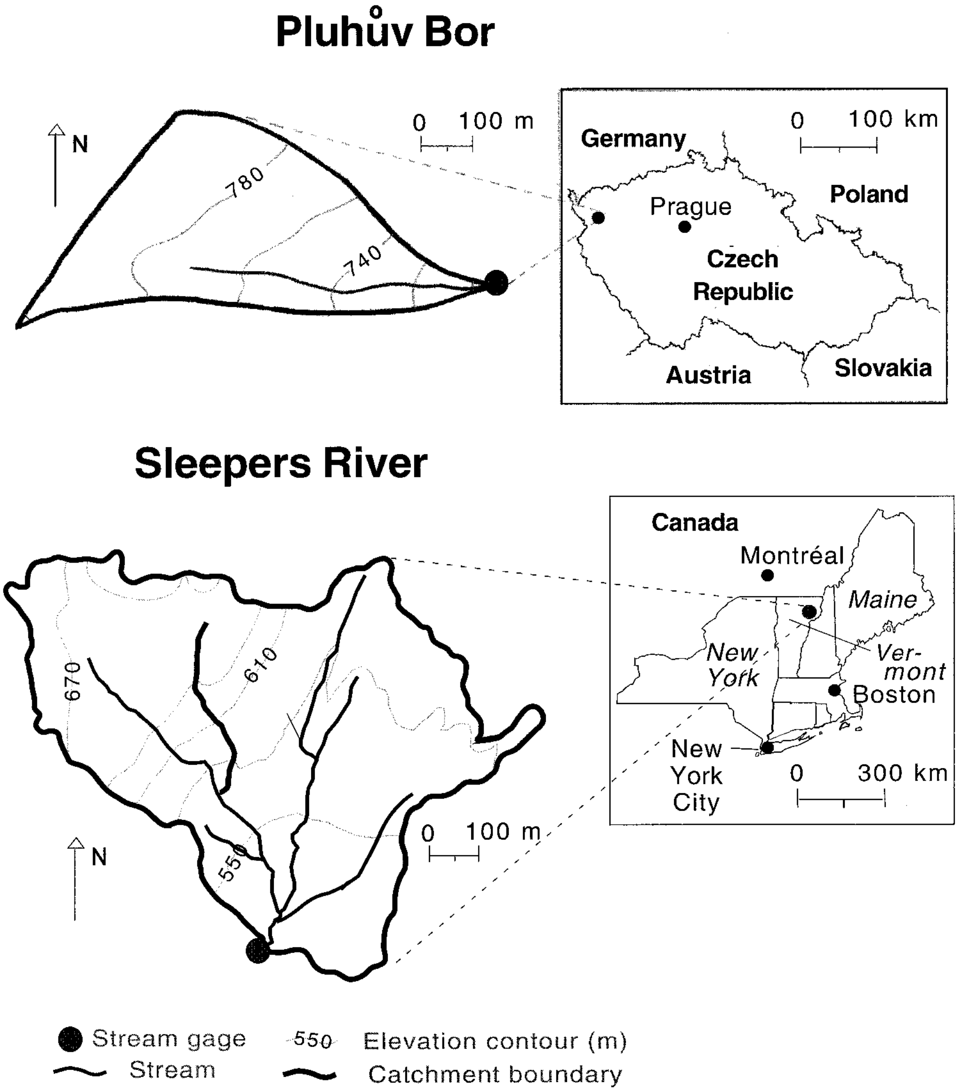

Figure 1. Location maps of (A) Pluhuv Bor, Czech Republic, and (B) Sleepers River W-9, Vermont, U.S.A.

2. Site Descriptions

Pluhuv Bor is a 22 ha catchment in the Slavkov Forest, western Bohemia, Czech Republic (Figure 1), ranging in elevation from 690 to 804 m (Table I). It is underlain by serpentinite, dominated by antigorite, an easily weathered magnesium (Mg)-silicate mineral that imparts high Mg and bicarbonate concentrations to drainage waters. Drainage waters are also high in sulfate (SO_4^{2-}) as a result of recent high sulfur (S) deposition. Apart from Mg, streamwater is very low in base cations,

TABLE I
Catchment comparison

	Pluhuv Bor	Sleepers River
Catchment area (ha)	22.0	40.5
Outlet elevation (m)	690	524
Relief (m)	114	155
Mean slope (%)	13	22
Aspect	SE	S
Annual average precipitation (mm)	910	1323
Annual average runoff (mm)	252	738
Annual average temperature (°C)	6.0	4.6
Vegetation	Norway spruce, with minor Scots pine	Sugar maple, yellow birch, white ash, American beech, red spruce, balsam fir
Bedrock	Serpentinite	Phyllite, calcareous schist
Soils	Inceptisols	Inceptisols, spodosols, histosols
Glacial deposits	None	1–4 m

reflecting the chemistry of the serpentinite. Pluhuv Bor was not glaciated during the last Ice Age. Brown earths and gleyey peats have developed to a depth of 0.5 to 4 m. The catchment is 94% forested by a 100 yr old plantation of mainly Norway spruce with a minor amount of Scots pine. The nonforested area is in grasses. Pluhuv Bor has a mean annual air temperature of 6 °C.

The U.S.A. site is the W-9 catchment at Sleepers River Research Watershed in northeastern Vermont (Figure 1). W-9 is a 40.5 ha catchment underlain by a quartz-mica phyllite with beds of calcareous granulite (Table I). Elevation ranges from 524 to 672 m. The Sleepers River watershed was glaciated and is mantled by 1–4 m of fairly dense basal till with a large percentage of fine silt. Inceptisols and spodosols have developed on the till in upland settings to an average depth of 70 cm. Histosols prevail in riparian zones and are characterized by as much as several tens of centimeters of black muck overlying the dense till. Swampy areas in headwater settings have as much as 2 m of peat. Weathering of calcite in the till leads to a calcium-bicarbonate-sulfate water. The SO_4^{2-} derives primarily from sulfides within the till and bedrock (Bailey *et al.*, in press). The forest cover is northern hardwoods dominated by sugar maple, yellow birch, white ash, and American beech. Softwoods make up about 15% of the basin and include balsam fir and red spruce. The forest was partially logged in 1929, and some additional yellow birch was removed in 1960. The mean annual temperature is 4.6 °C.

Several differences in the physical and chemical characteristics of these two catchments confound the effort to compare response to differential acid loading. The prominent differences, in order of descending importance, are (1) primary buffering by weathering of magnesium silicate (Pluhuv Bor) vs. calcium carbonate (Sleepers River); (2) hydrologic setting – 50% more precipitation and three times more runoff at Sleepers River, and evidence for greater importance of shallow flow paths at Pluhuv Bor; (3) glaciation at Sleepers River vs. none at Pluhuv Bor; and (4) planted coniferous forest at Pluhuv Bor vs. natural regeneration deciduous forest at Sleepers River. Despite these differences, these two sites are among the best-studied well-buffered catchments in the world and offer an excellent opportunity for comparison.

3. Results

3.1. Hydrology

Pluhuv Bor is a considerably drier environment than Sleepers River. Sleepers River W-9 catchment receives an annual average of 1320 mm of precipitation (25% as snow) compared to 950 mm at Pluhuv Bor (15% as snow) (Figure 2). Annual runoff averages 760 mm at Sleepers River and 270 mm at Pluhuv Bor. Evapotranspiration, calculated as the difference between precipitation and runoff, is 560 ± 40 mm at Sleepers River and 680 ± 150 mm at Pluhuv Bor. The greater evapotranspiration at Pluhuv Bor compared to Sleepers River reflects a longer growing season, with slightly warmer mean temperature and much shorter duration of snow cover. Runoff at Pluhuv Bor is greatest during the winter months, when precipitation is least, and least during the summer months, when precipitation is greatest. This pattern is driven by seasonal evapotranspiration demand, with some modification by storage and release from the snowpack. High runoff is sustained through the winter because of limited snowpack storage, and a modest runoff peak occurs in March from snowmelt. Runoff at Pluhuv Bor decreases to less than 10 mm mo^{-1} during the summer months. Compared to the nearby Lysina catchment, Pluhuv Bor has similar runoff in winter but less runoff in summer, consistent with its greater rooting depth.

The Sleepers River W-9 catchment has greater month-to-month variation in streamflow compared to Pluhuv Bor, despite a more uniform distribution of monthly precipitation (coefficient of variation for monthly precipitation was 18% compared to 33% at Pluhuv Bor). The greater hydrologic variation is due to a prominent influence of the seasonal snowpack at Sleepers River (Figure 2). Snow typically covers the landscape from mid-November until mid-April, and flow gradually recedes through the winter. Water stored in the seasonal snowpack is released during spring snowmelt, when approximately half of the annual runoff occurs during a 6 wk period from late March to early May. Streamflow recedes through the summer,

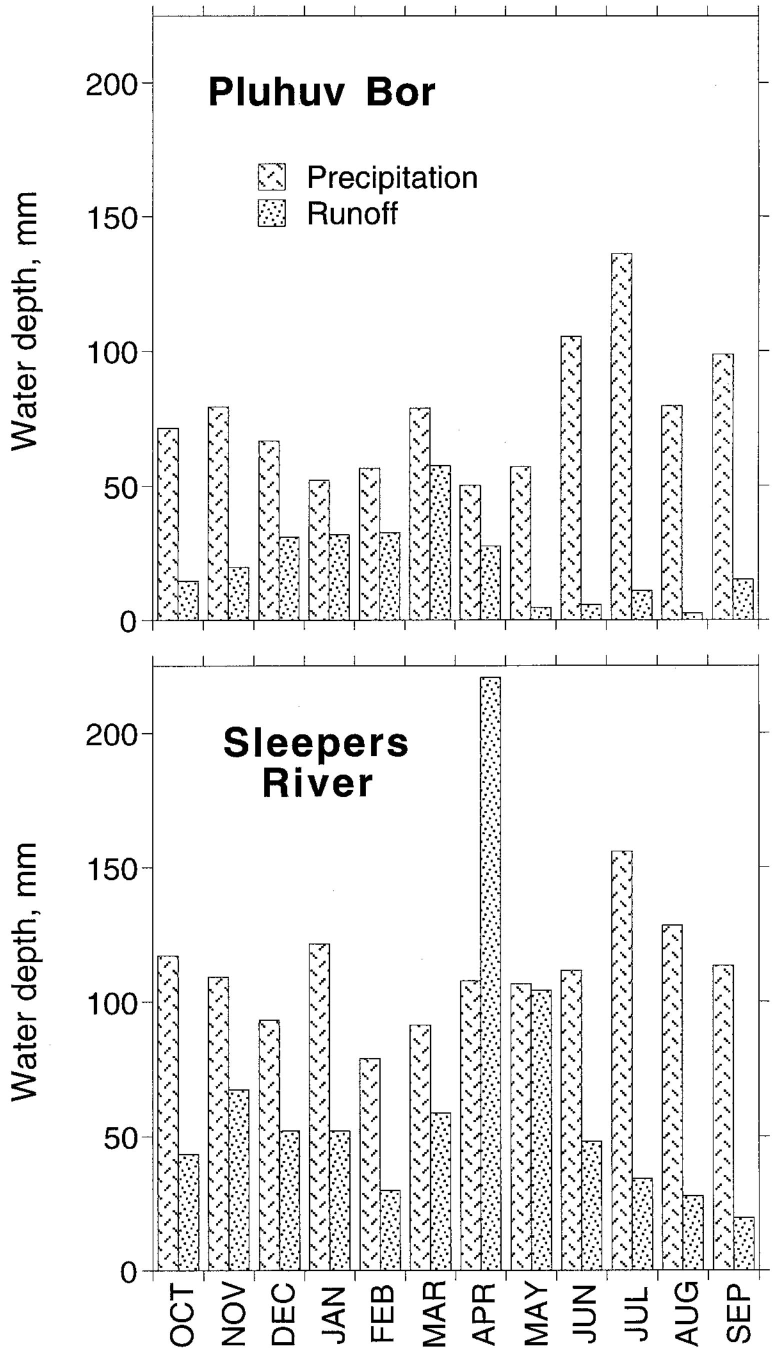

Figure 2. Mean monthly precipitation and runoff at Pluhuv Bor and Sleepers River W-9, 1991–1999.

punctuated by storms that may cause high peak discharges but that have limited duration. Low-intensity fall storms cause more significant runoff as the aquifer recharges. At Pluhuv Bor, the snowpack is less persistent and of shorter duration than at Sleepers River. Flow increases in winter due to reduced evapotranspiration and periodic rain and melt events. Event-driven flow increases occur occasionally at any time of year, but high flows are sustained for significant periods only during snowmelt. The smaller interannual variability of evapotranspiration at Sleepers River reflects the more consistent moisture supply relative to Pluhuv Bor.

At Sleepers River, groundwater makes the greatest contribution to streamflow, even during most high-flow events. Dunne and Black (1970) demonstrated that saturation overland flow is the main streamflow generation mechanism at Sleepers River, but isotopic data demonstrate that most of the overland flow is caused not by the rain or snowmelt triggering the event, but by discharge of displaced groundwater (Shanley *et al.*, 2002b). Melting snow on the expanded saturated areas in a fully recharged condition causes high and broad hydrograph peaks. During summer, high-intensity storms may also cause high discharge peaks, but they are short-lived because saturated contributing areas are small. At Pluhuv Bor, base flow is sustained by persistent groundwater discharge. Snowmelt is less important compared to Sleepers River. The overall drier and slightly warmer climate at Pluhuv Bor appears to limit the extent of saturated areas. However, response to rainfall is flashy; during events, chemical evidence suggests a large dilution by water following a shallow flow path. This water probably is some combination of channel interception, near-channel saturated overland flow, and shallow subsurface flow, possibly through macropores.

3.2. Acid Deposition

Acid deposition in central Europe peaked later and with greater severity than in eastern North America. In the present-day Czech Republic, sulfur dioxide (SO_2) emissions peaked in 1982 at 2.4 Tg a^{-1}. This represents only 7.5% of the peak SO_2 emission in the U.S.A. in 1973. On a per capita basis, however, the peak annual Czech emissions were more than 50% greater than the peak in the U.S.A. in 1969 (Figure 3). On an areal basis, the peak of Czech SO_2 emissions per unit area of land surface was 10 times that of the U.S.A. peak. Since the peak years, SO_2 emissions have declined sharply in the Czech Republic and gradually in the U.S.A. By 1999, SO_2 emissions in the Czech Republic were at 10% of the 1982 peak, and were only 1.7 times greater per unit area than in the U.S.A. Current S loadings range widely in the Czech Republic, but they average 5–15 kg ha^{-1} a^{-1} in the area of Pluhuv Bor (Czech Hydrometeorological Institute, 2001), similar to those in the eastern U.S.A.

Modern precipitation acidity (from bulk collectors near each site) is similar at Pluhuv Bor and Sleepers River. In particular, sulfate and hydrogen ion concentrations are nearly the same (Figure 4a). Pluhuv Bor has considerably higher

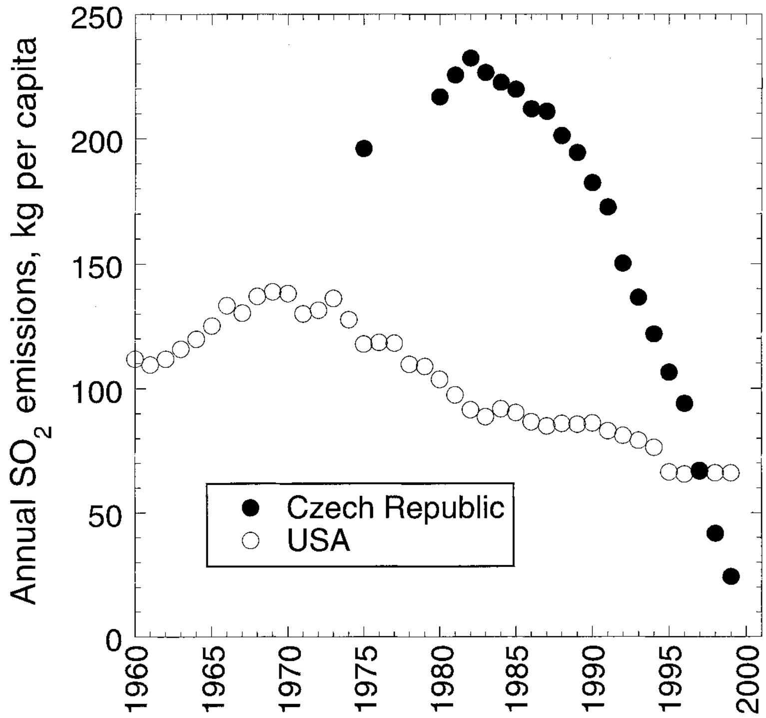

Figure 3. Plot of annual emissions of SO_2 per capita in the Czech Republic and U.S.A. Modified from Hruška *et al.* (2002); U.S.A. emissions data from U.S. EPA (2000).

chloride (Cl^-) and nitrate (NO_3^-) concentrations, balanced by greater base cation and ammonium (NH_4^+) concentrations. However, given the 50% greater precipitation amount at Sleepers River, SO_4^{2-} and H^+ loadings are greater at Sleepers River whereas NH_4^+ and NO_3^- loadings are similar at the two sites. Note that there is likely significant dry deposition input of both S and nitrogen (N) to these sites that is not captured in bulk deposition. Dry deposition of S may have a greater relative importance at Pluhuv Bor because of its proximity to point sources.

3.3. Stream chemistry overview

Acidic deposition is thoroughly neutralized at each site (Figure 4). Weathering of antigorite in the serpentinite at Pluhuv Bor gives rise to a Mg-bicarbonate water, whereas calcite weathering at Sleepers River leads to calcium bicarbonate streamwater. At both sites, base cations other than the dominant cation are minor contributors. In both catchments, SO_4^{2-} is the second most abundant anion. At Pluhuv Bor, high SO_4^{2-} concentrations reflect the legacy of high atmospheric S loadings, and a geologic source also may exist. At Sleepers River, where historical S deposition was considerably lower, SO_4^{2-} concentrations were lower than Pluhuv Bor despite an important geologic source of S in sulfide minerals.

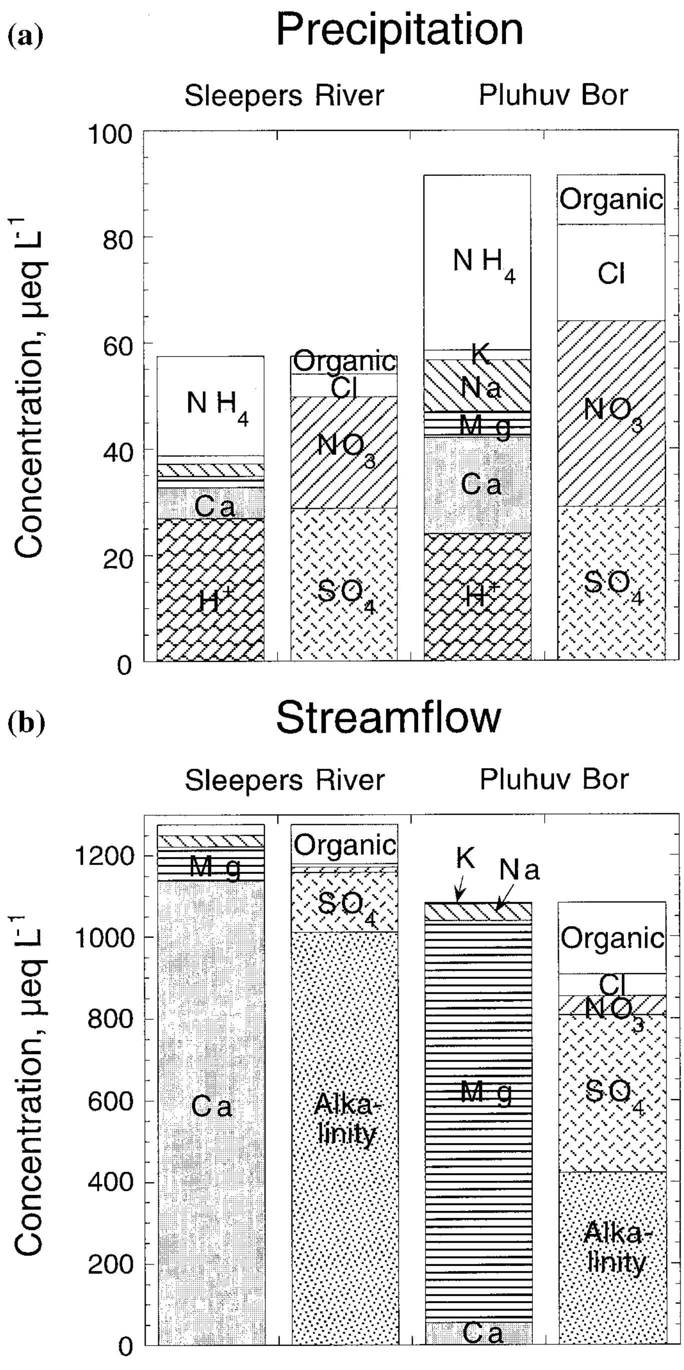

Figure 4. Major-ion chemistry of (A) precipitation and (B) streamflow of both catchments; mean annual concentrations based on water year 1999.

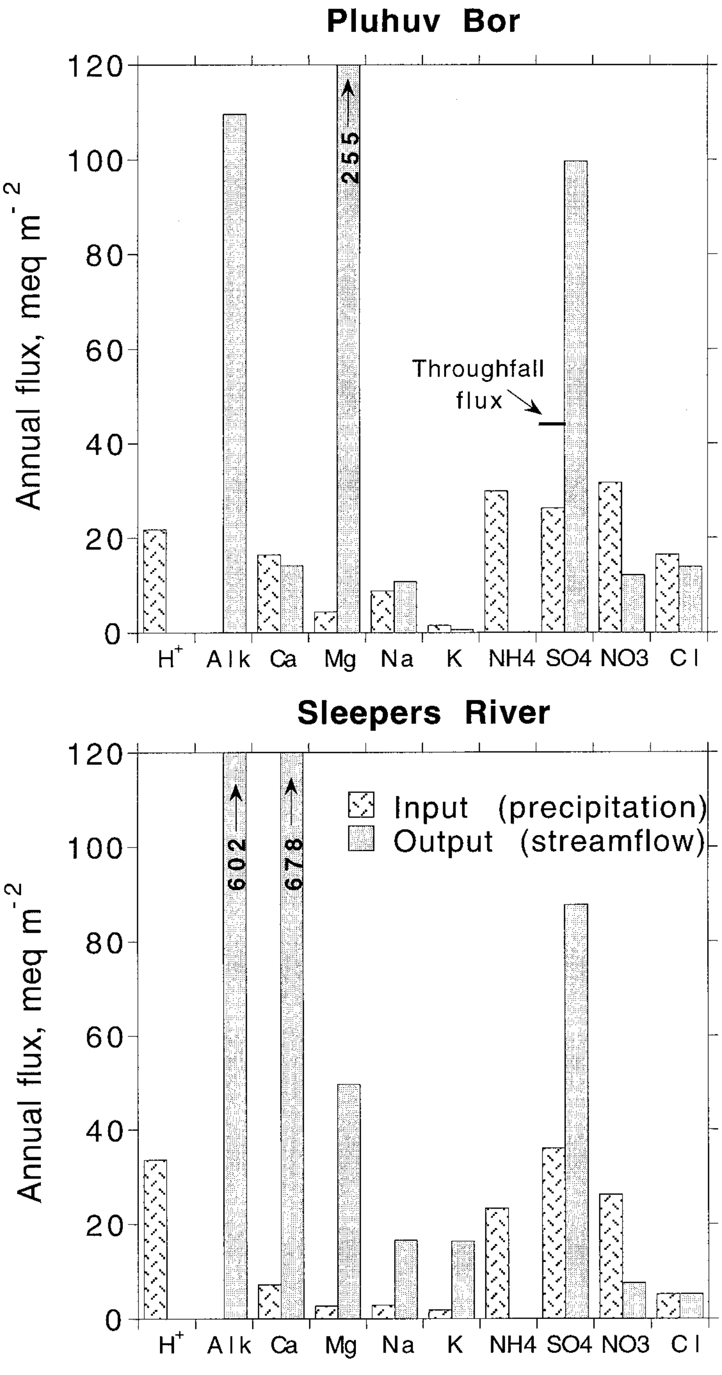

Figure 5. Chemical mass balance: Inputs in precipitation and outputs in streamflow at each site, based on water year 1999. Inputs based on bulk deposition, which may underestimate dry deposition, especially of sulfate. Sulfate deposition in throughfall is indicated for Pluhuv Bor. 'Alk' is alkalinity.

3.4. Input-output budgets

Because of the trends in atmospheric S deposition at Pluhuv Bor, we compare budgets for the two catchments during the most recent year with a complete data set, water year 1999. Input-output budgets (Figure 5) attest to the overwhelming ability of these catchments to buffer acidic deposition. On an annual basis, each catchment exports its dominant cation in amounts nearly two orders of magnitude greater than that cation in deposition and about one order of magnitude greater than the H^+ in deposition (charge basis). Secondary base cations at Pluhuv Bor are in approximate balance, suggesting little input from weathering and tight biogeochemical cycling of calcium (Ca) and potassium (K). At Sleepers River, in contrast, where Ca^{2+} is the dominant cation in streamwater, export of Mg is about 20 times the input, and sodium (Na^+) and K^+ also have a high net export. Net export of these secondary base cations is attributed primarily to the weathering of silicates, especially plagioclase.

The two catchments have similar mass-balance patterns for anions. In each catchment, Cl^- is in approximate mass balance, NO_3^- export is about half of NO_3^- deposition, and SO_4^{2-} export is about two times SO_4^{2-} deposition (assumed to be the sulfate flux in throughfall). Except for Cl^-, which has nearly 3 times higher flux at Pluhuv Bor, the magnitudes of the anion input/output fluxes are similar at the two sites. Contemporary S deposition is similar at the two catchments (Figure 5) despite differing trajectories of recent trends. Sulfate export exceeds input at Pluhuv Bor because past elevated S deposition is stored in catchment soil and biomass and is slowly released to surface water. In addition, there is evidence of a geologic S source at Pluhuv Bor (Krám *et al.*, 1997). At Sleepers River, young glaciated soils should have limited SO_4^{2-} adsorption capacity (Rochelle *et al.*, 1987), but most atmospheric S input appears to be incorporated in soil organic matter (J. Shanley *et al.*, unpublished data). In the absence of a strong atmospheric S deposition trend, soil incorporation of atmospheric S is probably balanced by mineralization of soil organic S. With some allowance for unmeasured dry deposition, the amount of net S export represents geologic S.

3.5. Trends in solute concentrations

Since atmospheric monitoring began in 1991, Pluhuv Bor has shown a modest declining trend in NO_3^- flux and a sharp declining trend in SO_4^{2-} flux in bulk deposition. Nitrate flux has decreased from about 45 to about 35 meq m^{-2} a^{-1}, while SO_4^{2-} flux has decreased from near 80 to about 30 meq m^{-2} a^{-1} during the past decade (Figure 6). For throughfall, SO_4^{2-} flux decreased from 220 to 50 meq m^{-2} a^{-1}, suggesting an even more rapid decrease in dry deposition of S. At Sleepers River, no trends are apparent in SO_4^{2-} or NO_3^- deposition during the same period.

In streamflow, there is no trend in NO_3^- concentration at either site. At Pluhuv Bor, the decline in mean streamwater SO_4^{2-} concentration, from greater than 1000

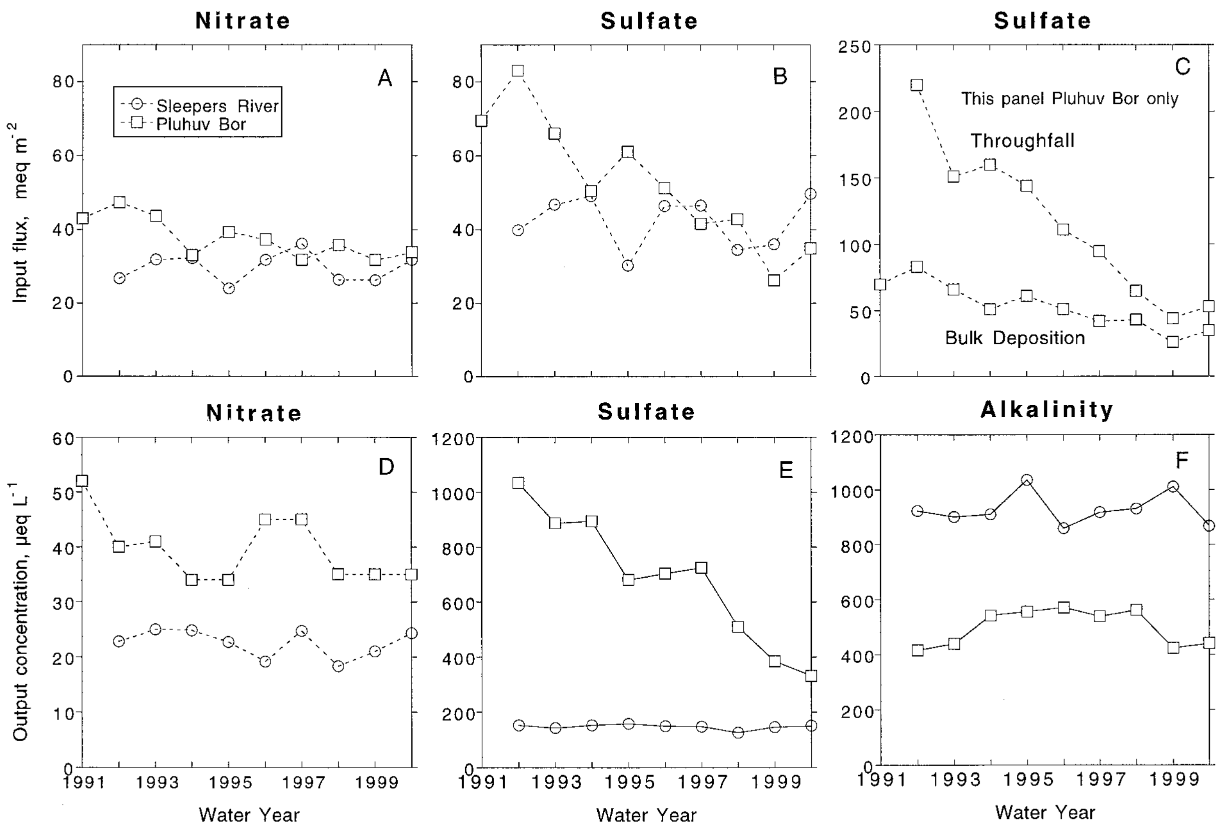

Figure 6. Chemical trends in the two catchments. Top row shows input fluxes in bulk deposition. Bottom row shows output concentrations in streamwater (concentrations rather than fluxes used for comparison purposes, to effectively normalize for interannual variation in flow). (A) Nitrate input. (B) Sulfate input. (C) Sulfate input in bulk deposition and throughfall at Pluhuv Bor. Difference attributed to dry deposition of S. (D) Nitrate output. (E) Sulfate output. (F) Alkalinity output.

μeq L^{-1} to less than 400 μeq L^{-1}, reflects the decrease in deposition. Mean annual SO_4^{2-} concentration in Sleepers River streamwater is remarkably constant near 170 μeq L^{-1}. Despite the declining trend in SO_4^{2-} concentration in Pluhuv Bor streamwater, there was no trend in alkalinity during the decade at either site (Figure 6).

3.6. Solute concentration variations with streamflow

Base cations show the characteristic dilution with increasing streamflow in both catchments. The range of concentrations, however, is greater at Pluhuv Bor (Figure 7). Absolute concentrations are a function of weathering rates and water residence times, but greater evapotranspiration at Pluhuv Bor contributes to the higher concentrations at low flow relative to Sleepers River. A greater dilution effect from precipitation may cause the occasional lower concentrations relative to Sleepers River. The surficial aquifer is presumably less areally extensive at Pluhuv Bor than at Sleepers River, so contributions to streamflow from direct channel precipitation, near-channel saturated overland flow, and shallow subsurface flow may assume greater importance.

As mentioned previously, these dilution episodes at Pluhuv Bor occasionally nearly deplete the alkalinity in this normally well-buffered catchment. The consistent input of groundwater at Sleepers River limits alkalinity depressions to about one-third of concentrations at low flow. The nondominant base cations at each site (Ca^{2+}, Na^{+}, and K^{+} at Pluhuv Bor and Mg^{2+}, Na^{+}, and K^{+} at Sleepers River) dilute with increasing flow similarly to the dominant cations and alkalinity.

In contrast to base cations and alkalinity, NO_3^- and DOC concentrations increase with increasing flow at each site. This is common behavior for these two solutes, which have a primary source in the forest floor from which they are flushed to streamwater during rain and snowmelt. As mentioned previously, the export of NO_3^- is about the same in the two catchments. DOC export averages 44 kg ha^{-1} a^{-1} at Pluhuv Bor compared to 13 kg ha^{-1} a^{-1} at Sleepers River. The spruce forest at Pluhuv Bor likely produces more DOC than the deciduous forest at Sleepers River.

Sulfate behavior displays the greatest contrast between the two catchments. At Sleepers River, SO_4^{2-} dilutes with increasing flow much like base cations and alkalinity (Figure 7). Sulfate and base cation concentrations co-vary at Sleepers River because most of the SO_4^{2-} in Sleepers River streamwater derives from weathering of sulfide minerals in the bedrock and till (Bailey *et al.*, in press). Sulfate does not behave as a strong acid anion because it is balanced by base cations. At Pluhuv Bor, by contrast, a large amount of anthropogenic SO_4^{2-} has been stored in the surface soil horizons, probably by adsorption. During high-flow events, this soil SO_4^{2-} is flushed to the stream. As at Sleepers River, there is also a deeper groundwater source of S at Pluhuv Bor. Although there is regional evidence of anthropogenic S leaking to the groundwater system (Lischeid *et al.*, 2002), the convergence of

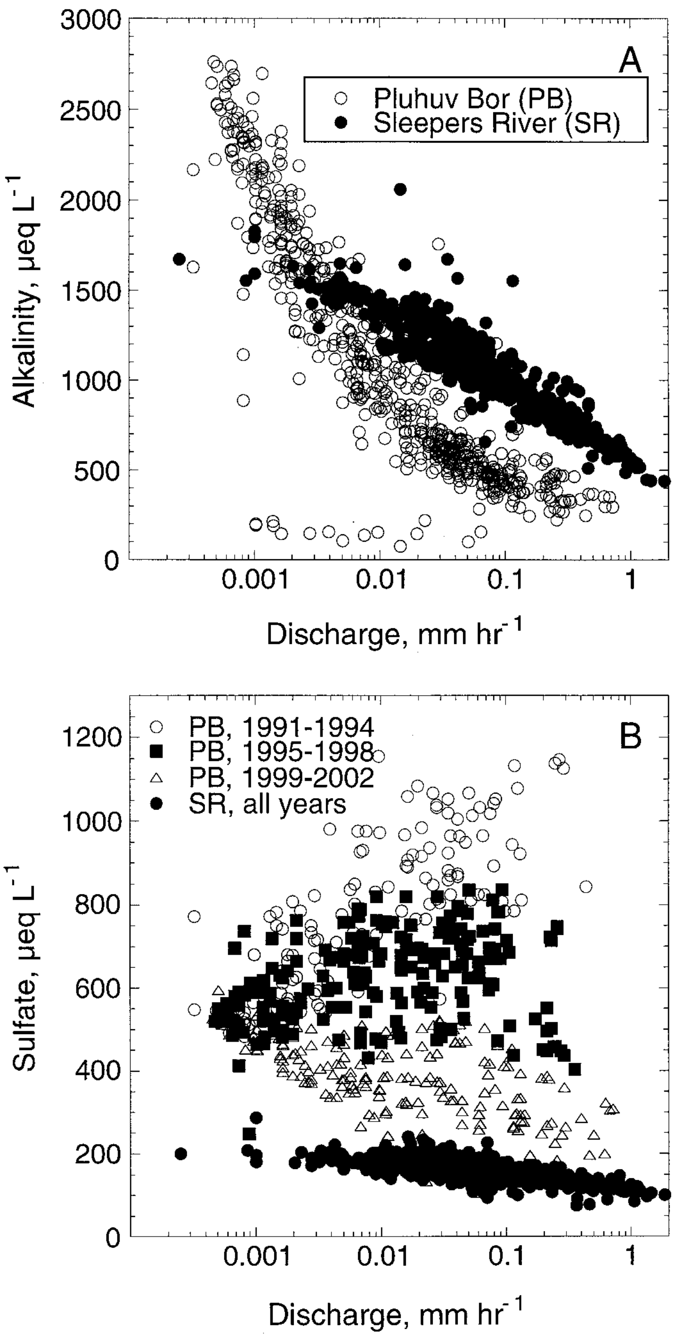

Figure 7. Concentration vs. discharge for (A) alkalinity, and (B) sulfate. Because of the strong declining trend in sulfate with time at Pluhuv Bor, sulfate data were split into three time periods, showing a shifting relation.

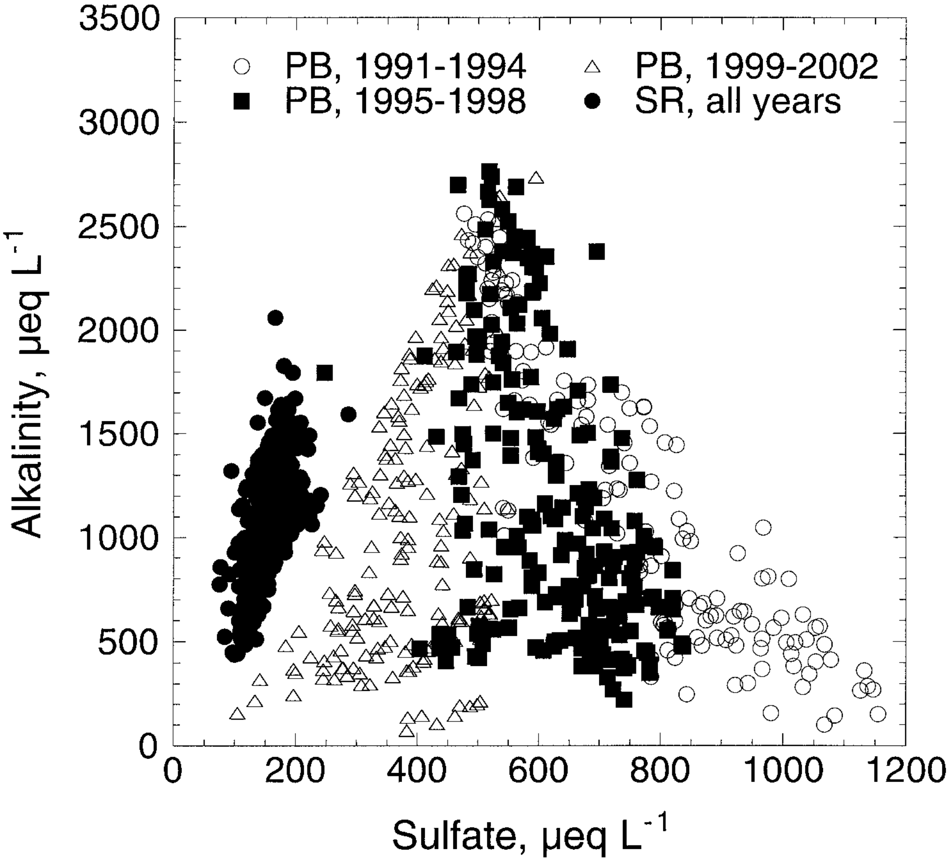

Figure 8. Sulfate vs. alkalinity for both sites. For Pluhuv Bor, data are split into three time periods.

low-flow SO_4^{2-} concentrations to a single value throughout a decade of sharply decreasing atmospheric S deposition argues for a geologic source. There is also independent evidence that this S may be geologic (Krám *et al.*, 1997). Streamwater SO_4^{2-} at Pluhuv Bor probably is a mixture of the deep and shallow sources, but because of the strong declining trend in SO_4^{2-} deposition over time, the soil SO_4^{2-} pool has become progressively depleted. The relation of SO_4^{2-} to flow therefore has shifted from positive in the early 1990s to negative at present, as soil-water SO_4^{2-} has shifted from higher to lower concentrations than SO_4^{2-} in groundwater, which remained constant through the period (Figure 7).

Similar to the relation of SO_4^{2-} to discharge at Pluhuv Bor, the relation between SO_4^{2-} and alkalinity has shifted from a positive to an inverse correlation during the same period (Figure 8). This unusual triangular distribution is formed by a series of mixing lines that move clockwise with time as soil S is depleted. The apex of the triangle represents the fixed endpoint SO_4^{2-} and alkalinity concentrations at base flow. Interestingly, the base of the triangle is horizontal, indicating that alkalinity depressions to near 100 μeq L^{-1} have occurred regularly throughout the period. These excursions are caused by dilution at high flows and are independent of the SO_4^{2-} dynamics. Although SO_4^{2-} was the acidifying compound in shallow soil water (e.g., decreasing soil base saturation), all SO_4^{2-} was neutralized completely within the soils and affected only the ionic strength of streamwater, not its acid/base character; otherwise, alkalinity depressions would be less severe at lower SO_4^{2-} concentrations. Alkalinity values at a given discharge were almost identical in the 'high SO_4^{2-}' period in the early 1990s and the 'low SO_4^{2-}' period in the early 2000s.

3.7. Forest health

If geology and forest type were similar at Sleepers River and Pluhuv Bor, it would be ideal to compare forest health under two different S loading regimes in similarly well-buffered catchments. However, outright comparison of forest health is confounded by differences in forest type, forest management practice, and geology. The method of forest health assessment also differed at each site, making comparison difficult. Despite the abundance of total cations from the weathering of serpentinite at Pluhuv Bor, the paucity of calcium is known to cause forest nutritional deficiencies on serpentinite landscapes (Roberts and Proctor, 1992).

The Norway spruce plantation at Pluhuv Bor exhibited opposing trends in two different indicators of forest health, as measured in 1994, 1996, and 2002 (P. Moravčík, Institute for Forest Ecosystem Research, Davle, unpublished data). The percentage of trees that exhibited some browning of needles decreased from 96% in 1994 to 50% in 2002. In contrast, average whole crown defoliation increased monotonically from 28 to 37% (19 to 27% if only the upper one-third of the crown is considered) during the period. As mentioned previously, Pluhuv Bor is outside the area of heaviest S deposition, and even forests on poorly-buffered lithologies in the Slavkov Forest have not experienced significant dieback. It is not clear why defoliation increased during a period when air quality was improving and SO_4^{2-} concentrations in soil water were decreasing.

Health of the northern hardwood forest at Sleepers River was assessed once in 2001 (R. Hallett, U.S. Forest Service, unpublished data). Percent branch dieback of dominant and codominant trees averaged from 5 to 15% in three separate stands. Crown vigor classification averaged 'healthy' in one stand, 'slight decline' in another, and intermediate between these two classes in the third stand. At both of these sites, weathering in the soil zone has depleted the buffering capacity, leading to surficial soil and soil solution pH less than 5 (Sleepers River: David and Lawrence, 1996; Pluhuv Bor: Krám *et al.*, 1997). Acidic soil conditions, possibly exacerbated by elevated S deposition, may be contributing to subpar forest health at both sites.

4. Discussion

Catchments with alkaline-weathering lithologies have received less study than their acid-sensitive counterparts. This study presents an opportunity to compare two of the best-studied well-buffered catchments. Because the Czech catchment has received higher acid loadings, we can evaluate the common assumption that easily weathered alkaline substrates provide 'infinite' buffering capacity. By comparing these two catchments, we have attempted to evaluate whether differing S loading has affected natural biogeochemical cycles in different ways.

Although present-day SO_4^{2-} export is comparable from the two catchments, the S source is primarily atmospheric at Pluhuv Bor (Krám *et al.*, 1997), whereas half or more of SO_4^{2-} comes from sulfide weathering at Sleepers River (J. Shanley *et al.*, unpublished data). However, because of the lower water flux, SO_4^{2-} concentrations average 3 times higher at Pluhuv Bor, and the range of SO_4^{2-} concentrations, even relative to the mean, is far greater. The high SO_4^{2-} loadings have acidified the soils and may be detrimental to forest health through both soil and atmospheric pathways. However, the deep alkalinity depressions at Pluhuv Bor result from hydrologic factors – namely, dilution by rain and snowmelt following shallow flow paths at high flow. The downward trend in SO_4^{2-} concentrations through time has been largely incidental to the acid/base status of the stream.

5. Conclusions

Pluhuv Bor in the Czech Republic and Sleepers River in Vermont, U.S.A. are both well-buffered catchments that currently receive mildly acidic deposition, but Pluhuv Bor has received much higher acid loadings in the recent past. Pluhuv Bor has a higher base flow alkalinity than Sleepers River but experiences episodic decreases in alkalinity during high flows, sometimes to 100 μeq L^{-1}, compared to 400 μeq L^{-1} at Sleepers River. Surprisingly, these decreases are not related to the S deposition, but rather to simple dilution. At Sleepers River, alkalinity depressions also are attributed to dilution, but they are less severe because of the sizeable groundwater contribution to streamflow. In well-buffered catchments such as these, episodic acidification will occur only by dilution of streamflow with a large volume of event water following shallow pathways where buffering is negligible.

Acknowledgements

This study was funded by the Grant Agency of the Czech Republic (Grant No. 205/01/1426) and by the U.S Geological Survey Water, Energy, and Biogeochemical Budgets (WEBB) Program. We appreciate the valuable reviews of Owen Bricker, Doug Burns, and an anonymous reviewer. Rich Hallett kindly provided forest health data.

References

Bailey, S. W., Mayer, B. and Mitchell, M. J.: 'The influence of mineral weathering on drainage water sulfate in Vermont and New Hampshire', *Hydrological Processes* (in press).

Czech Hydrometeorological Institute: 2001, *Air pollution in the Czech Republic in 2000*, Czech, Hydrometeorological Institute, Prague, Czech Republic, pp. 213.

David, M. B. and Lawrence, G. B.: 1996, 'Soil and soil solution chemistry under red spruce stands across the northeastern U.S.A.', *Soil Sci.* **161**, 314–328.

Driscoll, C. T., Lawrence, G. B., Bulger, A. J., Butler, T. J., Cronan, C. S., Eagar, C., Lambert, K. F., Likens, G. E., Stoddard, J. L. and Weathers, K. C.: 2001, 'Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies', *BioScience* **51**, 180–198.

Dunne, T. and Black, R. D.: 1970, 'An experimental investigation of runoff production in permeable soils', *Water Resour. Res.* **6**, 478–490.

Fottová, D. and Skořepová, I.: 1998, 'Changes in mass element fluxes and their importance for critical loads: GEOMON network, Czech Republic', *Water, Air, Soil Pollut.* **105**, 365–376.

Hruška, J., Moldan, F. and Krám, P.: 2002, 'Recovery from acidification in central Europe – Observed and predicted changes of soil and streamwater chemistry in the Lysina catchment, Czech Republic', *Environ. Pollut.* **120**, 261–274.

Kopáček, J., Veselý, J. and Stuchlík, E.: 2001, 'Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850–2000)', *Hydrol. Earth Sys. Sci.* **5**, 391–405.

Krám, P. and Hruška, J.: 1994, 'Influence of bedrock geology on elemental fluxes in two forested catchments affected by high acidic deposition', *Appl. Hydrogeol.* **2**, 50–58.

Krám, P., Hruška, J., Wenner, B. S., Driscoll, C. T. and Johnson, C. E.: 1997, 'The biogeochemistry of basic cations in two acid-impacted forest catchments with contrasting lithology', *Biogeochemistry* **37**, 173–202.

Lischeid, G., Böttcher, H., Krám, P. and Hruška, J.: 2002, 'Comparative analysis of hydrochemical time series of adjacent catchments by process-based and data-oriented modelling', in G. H. Schmitz (ed.), *Water Resources and Environmental Research, Vol. 2, Matter and Particle Transport in Surface and Subsurface Flow*, Technical University Dresden, Germany, pp. 237–241.

Novák, M., Bottrell, S. H., Fottová, D., Buzek, F., Groscheová, H. and Žák, K.: 1996, 'Sulfur isotope signals in forest soils in Central Europe along an air pollution gradient', *Environ. Sci. Technol.* **30**, 3473–3476.

Roberts, B. A. and Proctor, J. (eds): 1992, *The Ecology of Areas with Serpentinized Rocks: A World View*, Geobotany 17, Kluwer Academic Publishers, Dordrecht, pp. 427.

Rochelle, B. P., Church, M. R., and David, M. B.: 1987, 'Sulfur retention at intensively-studied watersheds in the U.S. and Canada', *Water, Air, Soil Pollut.* **33**, 73–83.

Shanley, J. B. and Chalmers, A. T.: 1999, 'The effect of frozen soil on snowmelt runoff at Sleepers River, Vermont', *Hydrol. Process.* **13**, 1843–1857.

Shanley, J. B., Schuster, P. F., Reddy, M. M., Roth, D. A., Taylor, H. E. and Aiken, G. R.: 2002a, 'Mercury on the move during snowmelt in Vermont', *EOS, Trans. Am. Geophys. Union* **83**, 45–48.

Shanley, J. B., Kendall, C., Smith, T. E., Wolock, D. M. and McDonnell, J. J.: 2002b, 'Controls on old and new water contributions to streamflow in some nested catchments in Vermont, U.S.A.', *Hydrol. Process.* **16**, 589–609.

U.S. EPA: 2000, *National Air Pollutant Emission Trends, 1900–1998*, U.S. Environmental Protection Agency, EPA-454/R-00-002, pp. 238.