

Rapid regional recovery from sulfate and nitrate pollution in streams of the western Czech Republic – comparison to other recovering areas

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Received 30 April 2004; accepted 19 October 2004

Acidified streams experienced unprecedented recovery from sulfate and nitrate pollution but pH and ANC decreased in alkaline streams.

Abstract

Hydrochemical changes between 1991 and 2001 were assessed based on two synoptic stream surveys from the 820-km² region of the Slavkov Forest and surrounding area, western Czech Republic. Marked declines of sulfate, nitrate, chloride, calcium and magnesium in surface waters were compared with other areas of Europe and North America recovering from acidification. Declines of sulfate concentration in the Slavkov Forest ($-30 \mu\text{eq L}^{-1} \text{yr}^{-1}$) were more dramatic than declines reported from other sites. However, these dramatic declines of strong acid anions did not generate a widespread increase of stream water pH in the Slavkov Forest. Only the most acidic streams experienced a slight increase of pH by 0.5 unit. An unexpected decline of stream water pH occurred in slightly alkaline streams.

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Keywords: Regional hydrochemistry; Stream survey; Acidification recovery; Sulfate; Nitrate

1. Introduction

To date most analyses of acidification recovery trends in Europe and North America have been based on studies of very large numbers of lakes (Skjelkvåle et al., 2001b) or dozens of intensively monitored small stream or lake catchments (Evans et al., 2001). Long-term monitoring is essential to verify that large investments in emission controls have resulted in better ecological conditions and that surface water chemistry is improving.

However, small catchments (less than 1 km²) are not necessarily representative of large regions. A dense regional network of stream sampling sites could improve spatial extrapolations of the results from lakes or small catchments.

Two regional surveys one decade apart provide the opportunity to assess changes in stream chemistry during a period of dramatic emission reductions in the westernmost part of the so-called Black Triangle region of Central Europe, a formerly extremely polluted area. The objective of this paper is to evaluate the decadal change in stream water pH and concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), sodium (Na^{+}), aluminum (Al^{3+}), iron (Fe^{2+}), arsenic (As^{2+}), beryllium (Be^{2+}), sulfate (SO_4^{2-}), nitrate (NO_3^-),

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chloride (Cl^-) and fluoride (F^-). The original geochemical survey of stream waters was conducted in 1991 at 148 sites in the Slavkov Forest, western Bohemia, western Czech Republic (CR). That sampling was part of a large geochemical mapping project for the entire area of the CR (Veselý et al., 1986). Maps of surface water chemistry showed the acidification status and contamination of streams by toxic metals when atmospheric deposition of sulfur and other anthropogenic pollutants in the CR had just started a significant decline from peak levels. The same sites in the Slavkov Forest were resampled in 2001 (Majer and Krám, 2002) enabling a rigorous evaluation of regional stream chemistry changes in response to the marked decline of industrial emissions during the 1990s (Hruška et al., 2002).

2. Methods and site description

2.1. Site description

The Slavkov Forest (Slavkovský les) is in western Bohemia, in the western part of the CR. It lies southwest of Karlovy Vary, and about 120 km west of Prague (Fig. 1). The region of the Slavkov Forest and part of the surrounding area (especially the western part of the Teplá Plateau) is preserved as a Protected Landscape Area. The area of the Slavkov Forest Protected Landscape Area is 610 km². The altitude of the area ranges from about 400 to 983 m a.s.l. Mean annual air temperature is between 5 and 7 °C and mean annual precipitation is between 600 and 1000 mm. The prevailing wind is from the west, with a southwestern component during winter and a northwestern component during summer. Southern winds are the least common. The forests consist primarily of plantations of Norway spruce (*Picea abies*) and deciduous trees occur

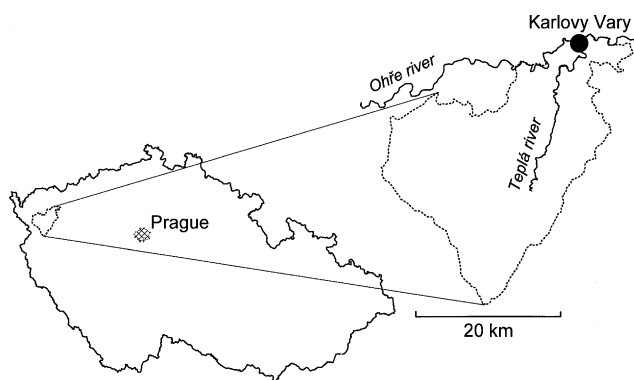


Fig. 1. Map of the Czech Republic, detailing the 610-km² Protected Landscape Area of Slavkov Forest (CHKO Slavkovský les) in western Bohemia. The total area of the synoptic surveys of stream waters in 1991 and 2001 was about 820 km².

only in the lowest areas. The remaining areas are used for fairly low-intensity agriculture. Abandoned underground tin mines are found in the central part of the study area.

Immediately north of the Slavkov Forest is a highly industrialized region, which includes chemical factories and large power production facilities using soft coal from nearby open-pit mines. The largest accumulation of coal-burning electric utilities in Europe occurs 70 km to the northeast. The northern slopes of the Slavkov Forest were exposed to very high atmospheric concentrations of SO_2 (usually above $60 \mu\text{g m}^{-3}$) between 1972 and 1991. From 1992 to 2000, atmospheric SO_2 concentrations decreased to less than $10 \mu\text{g m}^{-3}$. The central part of the Slavkov Forest had SO_2 concentrations near $30 \mu\text{g m}^{-3}$ between 1972 and 1991 and less than $5 \mu\text{g m}^{-3}$ in 1997–2000 (Šrámek and Balcar, 2001). Burning of soft coal has been the major source of SO_2 emissions with the peak in 1982. The decrease in SO_2 emissions was achieved by massive deployment of desulfurization equipment, which used the wet limestone scrubbing method. All Czech power plants were equipped with desulfurization technology between 1993 and 1999 (e.g. the closest power plant Tisová was equipped in 1995–1997).

In the early 1990s, political and economic changes in central and eastern Europe brought a focus on environmental quality that led to a rapid decrease of industrial emissions, especially of S in the heavily polluted Black Triangle area. The decline of anthropogenic emissions of SO_2 , NO_x and particulate matter in the CR is presented in Fig. 2. The extraordinarily steep decline of SO_2 ended in 1999, the year of the completion of the desulfurization equipment installations. The significant decline in emissions of particulate matter (especially fly ash) leveled out in the same year. In

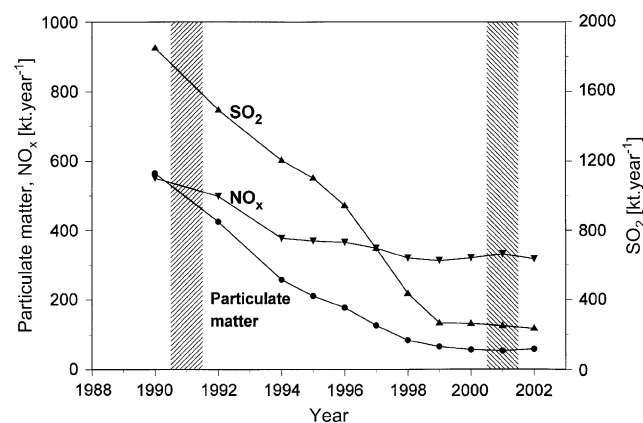


Fig. 2. Total emissions of major air pollutants (sulfur dioxide, nitrogen oxides and particulate matter) in the Czech Republic in 1990–2002 (Machálek et al., 2003). Dashed areas show the years of two regional surveys of the Slavkov Forest.

contrast, the decline of NO_x emissions was more modest. From 1991 to 2001, Czech emissions of SO_2 declined approximately by 85%, emissions of particulate matter declined by 90%, and emissions of NO_x declined by 35%. Further decreases of N input to the stream network occurred due to lower use of agricultural fertilizers after a decrease in state subsidies.

2.2. Field sampling

The surface water chemistry maps of the CR are based mainly on samples from small streams, partially supplemented by samples from rivers and occasionally also from reservoirs and springs (Veselý et al., 1986; Veselý and Majer, 1996). As part of the mapping project, systematic sampling at 148 sites in the Slavkov Forest and surrounding areas was conducted in 1991 (Majer et al., 1995). Sampling density depended on the topography, surface water drainage density and geology of the study area. Mean sampling density in the Slavkov Forest was about 1 sample per 5 km^2 . Altitude of the sampling sites ranged from 390 to 900 m a.s.l with a median altitude of 590 m a.s.l.

The second regional survey was performed in 2001 at exactly the same 148 sites representing small streams in the Protected Landscape Area (72% of samples) or in its immediate vicinity (28%). The total area of the survey was about 820 km^2 (Majer and Krám, 2002). The two survey years (1991 and 2001) were years with below average precipitation and without major hydrologic events. The regional stream sampling was conducted during summer baseflow hydrologic conditions in both Slavkov Forest surveys.

2.3. Laboratory analyses and statistical treatments

A standard collection, sample processing and analytical methodology was developed in the framework of the regional mapping of Czech surface waters (Veselý et al., 1986; Veselý and Majer, 1996). Specific conductance and pH (by glass electrode) were measured in the field on the day of sampling. All other measurements were performed later in the accredited laboratories of the Czech Geological Survey. Cation concentrations were determined by atomic absorption spectrophotometry (AAS). Flame AAS was used for major cations (Ca, Na, K, Mg, Al, Fe) and graphite furnace AAS was used for trace metals (As and Be) and for low concentrations of Al (2001 only). Concentration of F^- was determined by ion selective electrode. Concentrations of strong acid anions (SAA: Cl^- , NO_3^- and SO_4^{2-}) were determined by high-pressure liquid chromatography (HPLC) with conductivity detection. Acid neutralizing capacity (ANC) was calculated as the difference in the equivalent sum of base cations ($\text{SBC} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$)

and SAA as follows: $\text{ANC} = \text{SBC} - \text{SAA}$. ANC was used as an approximation of bicarbonate (HCO_3^-) concentration because equivalent concentrations of hydrogen ions, aluminum and anions of organic acids were typically small in comparison to SBC and SAA. The same analytical methods were used for both surveys. Laboratories of the Czech Geological Survey have regularly taken part in international inter-laboratory quality controls with very good results. Reproducibility was tested on field and laboratory duplicate samples during the regional study of the CR on 10% of the samples (Veselý and Majer, 1996).

Non-parametric analysis was used due to frequent asymmetry of the data distribution and due to the common occurrence of outliers. Values below detection limit were replaced by 0.4 times this limit for statistical treatment. Samples with extremely high Fe content ($> 2.5 \text{ mg L}^{-1}$) were excluded (because of the influence of particulate matter). Samples with extreme changes in As concentrations ($> 5 \mu\text{g L}^{-1}$) between surveys were excluded from the dataset of differences.

The edited datasets of stream water chemistry were evaluated by factor analysis (S-plus, MathSoft, USA). Factor analysis of major ion and trace element concentrations was performed separately on datasets from 1991 to 2001 surveys, as well as on a third dataset containing the differences of concentrations between the two periods. The factor analysis helps to identify main factors controlling chemical variability within each data set. The principal factor estimate with the varimax rotation of factor loading was used. The calculated factors represent the most important effects on variability of solutes tested in the data sets; the variance indicates the part of variability explained by each individual factor. The uniqueness for each variable reflects the portion of the variation not shared with the other variables.

Density plots representing smooth versions of histograms were constructed. Y-axis values of the plots showing population frequency were adjusted to the X-axis values such that the area under each curve equaled 1.0 (Silverman, 1986). The window for calculating moving averages was 21 samples centered at the actual value. All samples had the same weight in the calculation of moving averages.

3. Results

3.1. Comparison to the Czech mean concentrations

The median concentrations of individual ions from the Slavkov Forest survey was compared to the medians calculated from the regional mapping of the entire CR (Veselý and Majer, 1998) (Table 1). Comparison to the

Table 1

Comparisons of stream water solute concentrations from two sampling surveys in the Slavkov Forest (SF) to concentrations from the entire Czech Republic (CR)

Parameter	Median SF 1991	Median SF 2001	Difference SF 2001–1991	Ratio SF 2001/1991	Median CR 1985–1996	Ratio SF 1991/CR 1985–1996
Conductivity	254	224	–30	0.88	403	0.63
pH	7.27	7.20	–0.07	0.99	7.5	0.97
H ⁺	0.054	0.063	0.009	1.17	0.032	1.69
Na ⁺	344	357	13	1.04	513	0.67
K ⁺	64	71	7	1.10	102	0.63
Mg ²⁺	660	608	–52	0.92	889	0.74
Ca ²⁺	1090	971	–119	0.89	2196	0.50
SBC	2158	2007	–151	0.93	3700	0.58
Cl [–]	275	210	–65	0.76	505	0.54
NO ₃ [–]	118	57	–61	0.49	202	0.58
SO ₄ ^{2–}	856	561	–295	0.66	1096	0.78
SAA	1249	828	–421	0.66	1803	0.69
ANC	909	1179	270	1.30	1897	0.48
Al	<200	130	nd	nd	<200	nd
Fe	0.34	0.66	0.32	1.94	0.3	1.13
As	0.9	1.40	0.50	1.56	0.9	1.00
Be	0.08	0.06	–0.02	0.75	0.02	4.00
F	180	160	–20	0.89	170	1.06

Units are $\mu\text{eq L}^{-1}$ for major cations and anions, $\mu\text{g L}^{-1}$ for trace elements (Al, Fe, As, Be, F), $\mu\text{S cm}^{-1}$ for conductivity, and pH units for pH. Sum of base cations (SBC) was calculated from the individual medians as Na + K + Mg + Ca. Sum of strong acid anions (SAA) was calculated from the individual medians as Cl + NO₃ + SO₄. ANC (acid neutralizing capacity) was calculated as SBC–SAA.

CR values (mean altitude of the sampling points: 430 m a.s.l.) showed that surface waters of the Slavkov Forest exhibited lower ionic concentrations. The more dilute waters in the Slavkov Forest are partly a consequence of lower prevailing weathering rates as well as relatively sparse settlement of the study area. On the other hand, median values of major ions show that the Slavkov Forest has the same general water chemistry type as the CR as a whole: Ca–Mg–HCO₃–SO₄ (cations and anions representing more than 20% of the total sum of ions on an equivalent basis). Concentrations of Mg, Na and K were about two-thirds of the median Czech values, whereas concentrations of Ca were only half. Sulfate had the highest concentration among anions (excluding HCO₃ inferred from ANC) in the Slavkov Forest and was about three-quarters the median Czech value. Concentrations of chloride and nitrate were slightly above half of the median Czech values. Median concentrations of F in the Slavkov Forest were similar to the median of the CR.

The median pH in Slavkov Forest streams (7.3) was slightly basic, as acidic waters with pH < 5.5 and negative ANC formed only about 10% of the dataset. These acidic waters were situated exclusively at altitudes above 600 m a.s.l. and the most acidic streams were in the area of highest elevation underlain exclusively by granite. Concentrations of Fe and As were elevated in the 2001 Slavkov Forest survey, and concentrations of Be were substantially greater than the Czech median in both Slavkov Forest surveys.

3.2. Concentration changes in the period 1991–2001

The median acid–base status of surface waters in the Slavkov Forest did not change appreciably between 1991 and 2001. Distribution curves of pH from both surveys showed identical maxima (higher in 2001) in the neutral zone, fewer values near pH 4.5, and a surprising pH decrease in waters that were alkaline in 1991 (Fig. 3). The ANC of surface waters clearly shifted to greater values, though the general character of the distribution curve of ANC with its two maxima did not change. The sulfate and nitrate distribution curves showed a dramatic shift to lower concentrations (Fig. 3).

From 1991 to 2001, concentrations of the divalent cations (Ca, Mg) decreased by about 10% and concentrations of monovalent cations (Na, K) increased by 10% for K and 4% for Na (Table 1). Due to the significantly higher equivalent concentrations of Ca and Mg in comparison to Na and K, the resulting SBC decreased by 151 $\mu\text{eq L}^{-1}$. This decrease was significantly less than that of SAA (421 $\mu\text{eq L}^{-1}$), which led to an overall increase of ANC by 270 $\mu\text{eq L}^{-1}$. More than two-thirds of the SAA decline was caused by a decrease in sulfate concentration (295 $\mu\text{eq L}^{-1}$). The highest relative change, however, occurred for nitrate; its median concentration decreased by 51%, for a mean trend of $-6.1 \mu\text{eq L}^{-1} \text{yr}^{-1}$. A large decrease also was observed for chloride (Table 1). Concentrations of stream water fluoride in the study area were similar to the Czech mean value and they remained fairly steady.

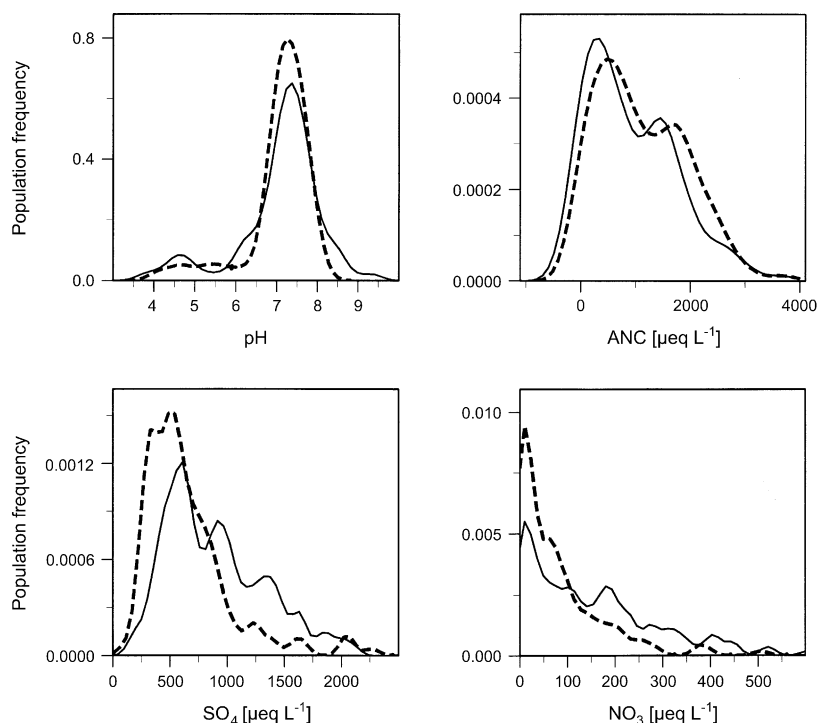


Fig. 3. Population frequency for pH, acid neutralizing capacity (ANC), sulfate and nitrate in 1991 (solid line) and 2001 (dashed line) surveys of stream waters in the Slavkov Forest. Y-axis values are adjusted to the X-axis values such that the area under each curve equals 1.

A slight regional decrease of F concentrations in streamwater was caused by a significant decrease of F in bulk precipitation and throughfall in 2001 relative to 1991, as documented at the Lysina catchment in the Slavkov Forest (Krám and Hruška, 2004).

The pattern of change in SBC, SAA and ANC varied as a function of the initial stream water pH in 1991 (Fig. 4). For waters with pH less than 7.5 in 1991, the decrease in SAA was greater than the decrease in SBC.

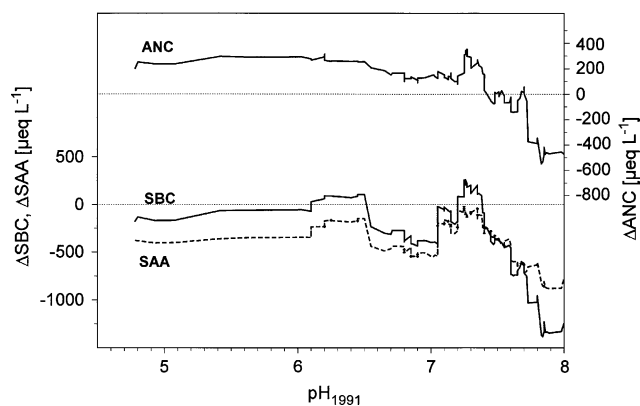


Fig. 4. Dependence of the concentration changes during 1991–2001 of strong acid anions (SAA = $\text{Cl}^- + \text{NO}_3^- + \text{SO}_4^{2-}$), base cations (SBC = $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) and acid neutralizing capacity (ANC = SAA – SBC) on the initial stream water pH during the 1991 survey. The data are presented as moving averages (width of window 21 samples).

On the other hand, for waters with pH greater than 7.5 in 1991, the decrease in SBC was greater than the decrease in SAA. Consequently ANC increased in waters with initial (1991) pH less than 7.5 and decreased in waters with initial pH greater than 7.5 (Fig. 4).

The change of pH in Slavkov Forest streams during the study period likewise depended on the original acid–base status in 1991. Increases in pH values were observed consistently in waters that had pH less than 7.0 in 1991 (Fig. 5). However, the pH of waters that had an initial pH greater than 7.5 in 1991 was usually lower during the second survey in 2001.

Concentrations of Fe and As in the Slavkov Forest in 1991 were similar to the median values for Czech surface waters (Table 1). Concentrations of these two metals increased markedly in the Slavkov Forest between the first and second survey. Sorption of As on Fe-oxyhydroxides has already been documented in the CR (Vesely and Majer, 1996). The median values increased by 94% for Fe and by 56% for As in 2001 in comparison to 1991. Changes of Fe and As concentration depended on the acid–base status of the original sample. Concentrations of As and Fe increased mainly in areas where the pH in 1991 was less than 6.8, with the greatest increases in the most acidic waters (Fig. 6). The increase was smaller in waters with initial pH greater than 6.8 in the Slavkov Forest.

Concentrations of Be in surface waters were markedly influenced by the acid–base status as expected

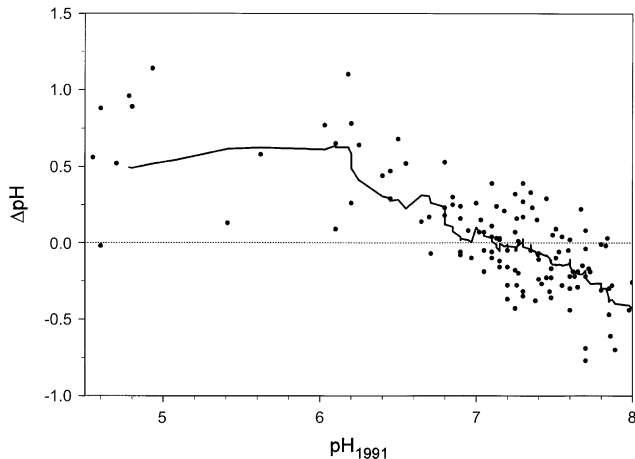


Fig. 5. Dependence of pH changes during 1991–2001 on the initial stream water pH during the first survey. The data are presented as moving averages (line, width of window 21 samples) and as individual samples (dots).

(Vesely et al., 2002b) and Be decreased with increasing pH (Majer and Krám, 2003). The highest concentrations of Be were found in high elevation areas with the lowest pH. Concentrations of Be were close to the detection limit ($0.02 \mu\text{g L}^{-1}$) in high-pH areas. However, the median Be concentrations changed only slightly (25% decrease, Table 1) because of the small changes in the median pH. Be increases and decreases at individual sites essentially tracked the pH shifts. Concentrations of Be decreased significantly at sites that had pH less than 6.5 in 1991; little change occurred at higher pH sites. Interpretation of Al patterns in the Slavkov Forest is limited because the 1991 samples were analyzed by flame AAS (Al detection limit 0.2 mg L^{-1}) rather than the more sensitive graphite furnace AAS. Al concentrations in samples with pH greater than 6.2 were generally below the detection limit of flame AAS. A strong negative relationship of Al with pH was evident for the pH range 3.7–6.2 in both surveys. Maximum concentrations of Al were greater than 1 mg L^{-1} in the 1991 survey, and near 0.9 mg L^{-1} in the 2001 survey. This decrease of Al concentrations relates to the increase of pH in the acidic range of the stream waters.

3.3. Major factors affecting stream water chemistry

The varimax rotated factor loadings for the four most important factors controlling surface water chemistry in the Slavkov Forest are given for all three datasets in Table 2. The variance of the individual factors varied between periods. The dominant factor in 1991 is marked by high loadings on concentrations of sulfate and divalent base cations and represented the influence of anthropogenic atmospheric deposition generated by coal burning. Its influence declined to fourth place in

2001, however it was the most important factor in the dataset of differences. Conversely, the fourth most important factor in 1991 represented the long-range atmospheric deposition of sea-salts (for Na and Cl), air pollutants (NO_x) from road traffic generating NO_3 and from agricultural fertilizers (NO_3 , K). This factor became the most important factor in 2001 and was the second most important factor in the dataset of differences. This factor controls the variability of concentrations of chloride and monovalent base cations (Na and K). The remaining two factors are related to the behavior of trace elements. Beryllium was influenced especially by acid–base reactions, both in the two period datasets and in the dataset of differences. Arsenic concentrations were mostly influenced by concentrations of F in the two period datasets. However, long-term changes of As were strongly linked to changes in Fe concentrations (fourth factor in the dataset of differences).

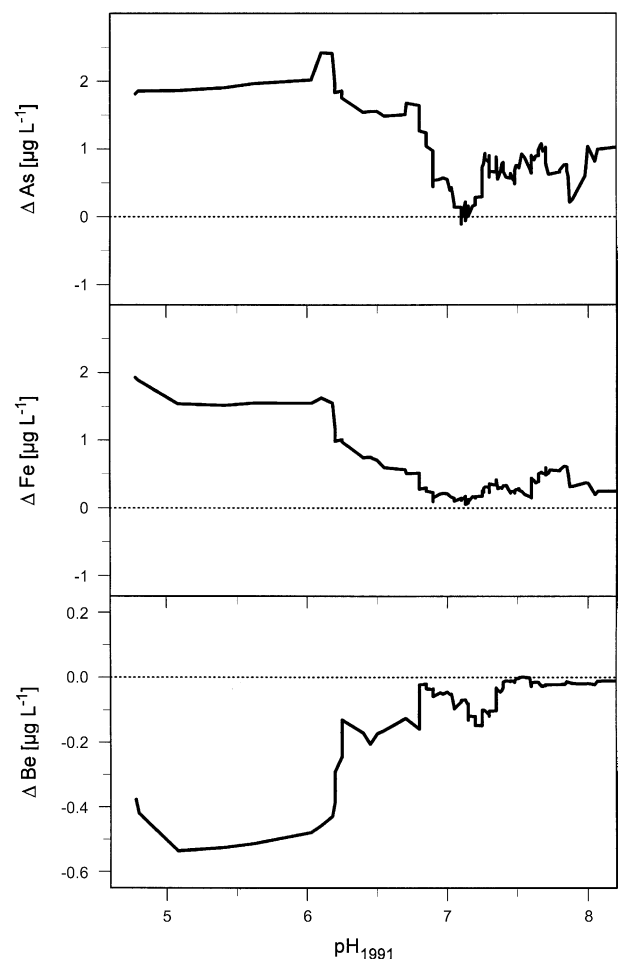


Fig. 6. Dependence of concentration changes during 1991–2001 of arsenic, iron and beryllium on initial stream water pH during the first survey. The data are presented as moving averages (width of window 21 samples).

Table 2

Factor loadings for the first four factors (F1–F4) of individual variables, identified by means of a factor analysis performed on the datasets from two synoptic regional surveys of stream waters in the Slavkov Forest in 1991 and 2001 and in the dataset of differences

Variable	1991 (139 Samples)					2001 (132 Samples)					Differences (123 samples)				
	F1	F2	F3	F4	U (%)	F1	F2	F3	F4	U (%)	F1	F2	F3	F4	U (%)
pH			0.85		17.4		0.93			11.3			–0.60		53.2
Ca	0.78				15.7				0.50	0.1	0.98				0.1
Mg	0.79				17.2		0.55			55.6	0.93				4.9
Na				0.86	2.1	0.72				0.1		0.67			31.1
K					54.4	0.74				37.4		0.55			47.4
Fe					55.8					73.0				0.63	56.1
As		0.85			25.8			0.80		35.5				0.65	52.3
Be			–0.80		25.0		–0.83			21.4			0.86		21.9
NO ₃					56.3	0.69				51.0					53.5
SO ₄	0.78				26.4				0.89	3.3	0.75				3.7
Cl				0.71	8.5	0.85				17.0		0.92			8.7
F		0.98			0.1			0.82		20.9					76.8
V (%)	19.8	15.2	14.5	12.1		22.1	18.5	12.7	11.4		23.0	14.9	9.9	7.3	

Variance explained by each factor (only values >0.5 are shown) and uniquenesses for each variable are presented. Samples with high Fe concentration (>2.5 mg L⁻¹) were excluded from the dataset. Samples with a high change in As concentrations (>5 µg L⁻¹) were excluded from the dataset of differences. V(%) represents percentage of total variance explained by the single factor. U(%) represents uniqueness, which is a fraction of the variance of single variables not explained by the factors.

4. Discussion

4.1. Atmospheric deposition

Throughfall fluxes of sulfate decreased more than bulk precipitation fluxes in the GEOMON network (Fottová and Skořepová, 1998; Fottová, 2003) of 14 intensively monitored forested catchments in the CR (including Lysina and Pluhův Bor in the Slavkov Forest). Atmospheric deposition fluxes of S and N varied widely in the GEOMON catchments in 1994–2001. This broad range in responses demonstrated that impacts of desulfurization measures implemented in the Czech power plants in the 1990s were less uniform than expected. Areas inside or close to the so-called Black Triangle region were influenced preferentially by desulfurization (Peters et al., 1999; Hruška and Krám, 2003). However, catchments at a larger distance from the desulfurized power plants (mainly in the Eagle Mountains, eastern Bohemia) experienced little change in S and N deposition (Fottová, 2003).

4.2. Surface water pH

The pattern of pH changes in surface waters in the Slavkov Forest was similar to the pattern recently observed in four other mountainous areas of the CR (Veselý et al., 2002a) and interestingly nearly two decades ago in Sudbury, Canada (Keller and Pitblado, 1986) as well. Veselý et al. (2002a) investigated four Czech regions with a total area of 1611 km². They sampled 432 streams (175 in the Ore Mts., 103 in the Eagle Mts., 98 in the Jizera Mts., and 56 in the Giant Mts.) in areas dominated by granite or gneiss bedrock.

The median altitude of the sampling points of the four regions ranged from 515 to 860 m a.s.l. The streams were sampled first in the period 1985–1986, and then a second time in the period 1996–2000. Stream water medians of SO₄, NO₃ and Cl concentrations decreased in a significant but fairly heterogeneous manner. The highest percentage change occurred for nitrate and chloride (Veselý et al., 2002a). Stream water pH increased in streams having pH less than 6.5 in 1985–1986. For streams with pH near 5 in 1985–1986, pH medians increased slightly more than one pH unit. In contrast, streams with pH greater than 6.5 in the first survey showed a significant decrease in pH in the second survey. Veselý et al. (2002a) summarized plausible explanations for this opposite behavior of waters with high pH: base cations decreased faster than acid anions decreased; biological uptake of major nutrients (N and base cations) increased; DOC increased preferentially in higher pH systems causing acidification by rising weak organic acid concentrations; and soil adsorption of base cations increased.

Changes in SAA probably were more related to changes in atmospheric deposition fluxes than were changes in SBC, which were more influenced by leaching from soils and vegetation. The pH of precipitation and particularly throughfall increased markedly in the Slavkov Forest during the study period (Krám and Hruška, 2004). The higher pH of these input waters may have resulted in a significant decrease in leaching of SBC from foliage and soils, especially in catchments with slightly alkaline drainage water pH. Decreased internal cycling of SBC in the 1990s was described in two intensively monitored catchments (Lysina and Pluhův Bor) in the Slavkov Forest (Krám and Hruška, 2004). In

this scenario, a consequence of the reduced leaching of SBC is that SBC decreased more rapidly than SAA concentrations in runoff, resulting in a pH decrease in the more alkaline streams during the last decade.

The pH changes in the Slavkov Forest followed a pattern similar to earlier changes in the Sudbury area lakes (Ontario, Canada) described by Keller and Pitblado (1986). Exceptionally large reductions in S emissions from ore smelters occurred at Sudbury. As a result, pH increased sharply in the period 1974/1976–1981/1983 in the more acidic lakes with pH 4.3–5.5. No consistent pattern was evident for the near-neutral lakes and, in contrast, several high-pH lakes (pH 7.5–8.5) exhibited a lower pH in the later surveys. Keller and Pitblado (1986) explained this phenomenon by the simple fact that the more acidic lakes were located relatively close (within 100 km) to the Sudbury smelters. However, the previously discussed processes hypothesized to explain pH decreases in the Czech streams may also hold for the Sudbury area lakes.

4.3. Surface water sulfate and base cations

Because of the relatively large distance from the sea, input of marine sulfate is low in central Europe and therefore non-marine sulfate is often considered equal to total sulfate (Evans et al., 2001; Prechtel et al., 2001; Alewell et al., 2001). The marine SO_4/Cl ratio of seawater. Marine sulfate was calculated to be only 2% of the sulfate in total atmospheric deposition at Lysina (Krám and Hruška, 2004). This proportion is probably representative for the whole Slavkov Forest.

Marked decreases in surface water non-marine sulfate concentrations were observed throughout Europe, confirming a positive response to reductions in anthropogenic S. The largest median decreases of sulfate detected at sites of the RECOVER: 2010 Project occurred in the glacial mountain lakes of Slovakia (High Tatras, $-4.2 \mu\text{eq L}^{-1} \text{yr}^{-1}$) and the Czech Republic (Bohemian Forest, $-3.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$; Evans et al., 2001, Fig. 7). The greatest median ANC increase ($+4.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$) from the European regions evaluated by Evans et al. (2001) was observed in the Bohemian Forest lakes. This increase was much smaller than the ANC increase in the Slavkov Forest region ($+27 \mu\text{eq L}^{-1} \text{yr}^{-1}$) or in the small catchments Lysina and Pluhův Bor ($+15$ and $+35 \mu\text{eq L}^{-1} \text{yr}^{-1}$, respectively; Krám et al., 2002).

Catchment response to decreased S deposition was very heterogeneous, as shown by an analysis of 20 European catchments (Prechtel et al., 2001). Sulfate decreased quickly in several Scandinavian streams and in all Czech (Vesely et al., 1998) and Slovak glacial lakes (Kopáček et al., 1998, 2001) containing young and thin soils in their catchments and thus exhibiting low sulfate

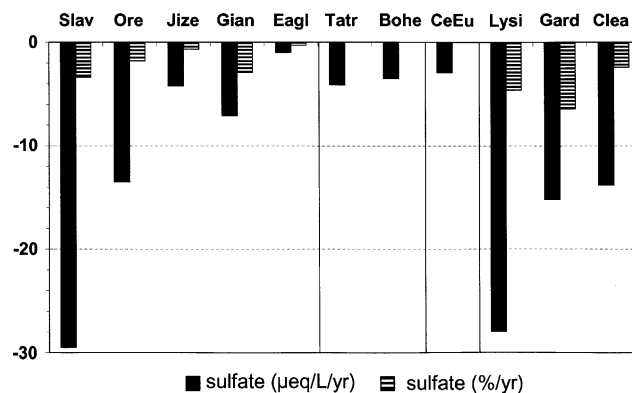


Fig. 7. Annual rates of long-term decline of sulfate concentrations in surface waters. Left panel: stream waters in the Slavkov Forest (1991 vs. 2001, this study); stream waters in the Ore Mts. (1985 vs. 1997), Jizera Mts. (1986 vs. 1996), Giant Mts. (1985 vs. 1997) and Eagle Mts. (1986 vs. 2000), Czech Republic (Vesely et al., 2002a); middle panels: lake waters in the High Tatras, Slovakia (1984–1999) and Bohemian Forest, Czech Republic (1984–1999) (Evans et al., 2001), Central European ICP-Waters sites (1989–1998, Skjelkvåle et al., 2001b); right panel: Lysina catchment in the Slavkov Forest (1991–2001, Krám et al., 2002), Gårdsjön F1 catchment, Sweden (1990–1999) (Moldan et al., 2001), and Clearwater Lake, Canada (1973–1999, Gunn, 1995; Jeffries et al., 2003).

storage capacity. However, the decrease in stream water sulfate was significantly delayed in German catchments with old, deeply weathered soils and a high soil pool of adsorbed sulfate. The delayed response was attributed to desorption of previously stored sulfate and by excess mineralization of organically bound S (Prechtel et al., 2001). Further evaluations using time series from 1987/1988 to 1999 at nine catchments of the low mountain ranges of Germany confirmed these delayed responses (Alewell et al., 2001). Sulfate concentrations in these streams decreased only slightly, while pH and ANC (and nitrate) were unchanged. Therefore, no significant acidification reversal was noted in Germany.

Significant downward trends in sulfate and base cation concentrations from 1989 to 1998 were apparent in surface waters of the international 98-site ICP-Waters network (Skjelkvåle et al., 2001b). The largest increases in ANC and pH occurred in waters of the most acidic class with negative ANC similar to the regional observations from the CR discussed previously (Vesely et al., 2002a; Majer and Krám, 2002; this study). A subpopulation of Central European ICP-Waters sites ($n = 34$) showed the following significant changes in concentrations: sulfate $-3 \mu\text{eq L}^{-1} \text{yr}^{-1}$ (Fig. 7), nitrate $-1 \mu\text{eq L}^{-1} \text{yr}^{-1}$, ANC $+1 \mu\text{eq L}^{-1} \text{yr}^{-1}$, SBC $-2 \mu\text{eq L}^{-1} \text{yr}^{-1}$ (Skjelkvåle et al., 2001b). The majority of 344 monitored Scandinavian lakes showed annual declines of non-marine sulfate in the range of $2\text{--}7 \mu\text{eq L}^{-1} \text{yr}^{-1}$. Some lakes in southernmost Sweden experienced pronounced decreases of up to $28 \mu\text{eq L}^{-1} \text{yr}^{-1}$ (Skjelkvåle et al., 2001a). The intensively monitored Gårdsjön F1

catchment in southwestern Sweden exhibited the fastest recovery from sulfate pollution ($-15.2 \mu\text{eq L}^{-1} \text{yr}^{-1}$, Fig. 7, Moldan et al., 2001) of all published (e.g. Evans et al., 2001) western European stream water trends in the 1990s. Note that three other Swedish catchments were erroneously reported to have even sharper sulfate declines (Moldan et al., 2001) but the trends were actually three times lower than published (Krám, unpublished data). The corrected largest decline of sulfate among these three Swedish catchments was $-9.4 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the 1990s (for the Berg-Pipbäcken Nedre catchment; Krám et al., 2001).

In the USA, downward trends in stream water sulfate were much smaller than in the CR or Scandinavia. Trends were evaluated in the Hydrologic Benchmark Network of US Geological Survey in the northeastern USA between 1984 and 1996. The largest sulfate decline ($-0.6 \mu\text{eq L}^{-1} \text{yr}^{-1}$) was observed in Ohio and the corresponding decline of divalent base cations was $-0.3 \mu\text{eq L}^{-1} \text{yr}^{-1}$ (Clow and Mast, 1999). In contrast, lakes in the vicinity of the Sudbury ore smelters, Ontario, Canada experienced world-renowned acidification recovery. The main source of sulfur in the processed ores was pyrrhotite (FeS). Sulfur emissions from the smelters decreased by 92%, from 2560 kt yr^{-1} in 1960 to 216 kt yr^{-1} in 1994 (Gunn, 1995). The Sudbury lakes showed a generally consistent pattern during this period of decreasing concentrations of sulfate, SBC and metals, and corresponding increases in pH and ANC. The most striking example was Clearwater Lake (0.8 km²), located 13 km from Sudbury, where sulfate decreased from 580 $\mu\text{eq L}^{-1}$ in 1973 to 220 $\mu\text{eq L}^{-1}$ in 1999 ($-14 \mu\text{eq L}^{-1} \text{yr}^{-1}$; -2.4% per year; Fig. 7), while pH increased from 4.3 in 1973 to 6.2 in 1999 (Dillon et al., 1986; Gunn, 1995; Jeffries et al., 2003). At the five Killarney Park lakes near Sudbury, sulfate decreased by 50% in about 30 yr (Keller et al. 2003).

4.4. Surface water chloride

Chloride, which is primarily derived from sea-salts, exhibited few long-term trends in the 1990s throughout Europe (Evans et al., 2001). However, Moldan et al. (2001) noted a significant decrease in Cl concentrations in runoff at nine intensively monitored Scandinavian catchments. The decrease was attributed to the large sea-salt inputs that occurred early in the 1990s. Skjelkvåle et al. (2001a) also reported a decrease of Cl during the 10-yr period 1990–1999 in about one-quarter of Scandinavian lakes. Deposition inputs of sea-salts including Cl are cyclic over several years due to the climatic influence of the North Atlantic Oscillation. Much of the Cl trend was attributed to anomalously high Cl deposition in 1993 in Norway and in 1989 in Sweden due to strong oceanic storms (Skjelkvåle et al., 2001a).

In central Europe Veselý et al. (2002a) reported a 23% ($17 \mu\text{eq L}^{-1}$) decrease of Cl in stream water in four Czech mountain ranges in the period 1985/1986–1996/2000. They noted that during the same period, Czech emissions of industrial Cl (as HCl) decreased by an estimated 50%. Therefore, the regional decrease of stream Cl was not caused by decreasing marine aerosol deposition of Cl, which was very small according to Veselý et al. (2002a). However, non-marine fractions of sulfate and base cations are commonly calculated under the assumption that all chloride is of marine origin and is accompanied by other ions in the same proportions as in sea water (Skjelkvåle et al., 2001a). Such calculations are standard even for sites far inland from the coast (Werner and Spranger, 1996). According to the Czech Hydrometeorological Institute database (CHMI, 2003) the annual industrial emissions of chlorine in the Czech Republic were highly variable but showed no downward trend between 1985 and 1999. Moreover, the reported average annual industrial chlorine emissions in the Czech Republic (38 t) were small and represented less than 1% of the total areal atmospheric deposition of chloride. This small percentage calls into question the completeness of the CHMI database. Therefore the reason for the large decline of chloride ($6.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$; $-2.4\% \text{yr}^{-1}$) in the region of Slavkov Forest remains unresolved.

4.5. Surface water nitrate

The median stream nitrate concentration decreased by 5% per year or $6 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the period 1991–2001 in the Slavkov Forest. A long-term pattern of persistent decrease of nitrate concentrations in stream water and shallow ground water was observed also in the Lysina catchment (Krám and Hruška, unpublished data). Decreases in stream water concentrations of nitrate between 1991 and 2001 were probably driven by biotic processes, especially by tree uptake and immobilization of nitrogen. This explanation is supported by tree ring analyses from the center of the Slavkov Forest at Lazy, at the Level Two Plot of the ICP-Forests network. Growth increments were suppressed in the period 1971–1989, probably as a result of the peak pollution levels during that period. Tree ring widths increased starting in the 1990s, as acidic atmospheric deposition decreased and fairly favorable growing-season meteorologic conditions prevailed (Šrámek et al., 2000).

Nitrate decreased by $5 \mu\text{eq L}^{-1} \text{yr}^{-1}$ or 4% per year in the survey of Veselý et al. (2002a) of the four Czech mountain ranges (Fig. 8). Veselý et al. (2002a) noted that this rapid decrease in nitrate concentrations in streams was surprising and probably unprecedented in the scientific literature. These decreases were comparable to those in the Slavkov Forest (Fig. 8). The

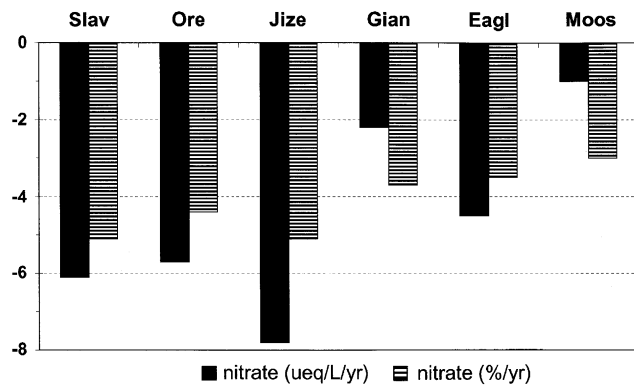


Fig. 8. Annual rates of long-term decline of nitrate concentrations in surface waters. Stream waters in the Slavkov Forest (1991 vs. 2001, this study); stream waters in the Ore Mts. (1985 vs. 1997), Jizera Mts. (1986 vs. 1996), Giant Mts. (1985 vs. 1997) and Eagle Mts. (1986 vs. 2000), Czech Republic (Vesely et al., 2002a), and Mt. Moosilauke region, New Hampshire, USA (1973/1974 vs. 1996/1997) (Goodale et al., 2003).

pronounced decrease in stream nitrate in the Czech mountains, which exceeded the decrease in N emissions, may have been caused by increased N uptake by vegetation in catchments undergoing acidification recovery, and/or by decreased mineralization of organic matter in forest soils in the late 1990s relative to the 1980s, when spruce decline (and increased litterfall) in the four Czech mountain areas culminated (Vesely et al., 2002a).

In European surface waters, nitrate concentrations have had a highly variable pattern and much weaker trends compared to sulfate since the 1980s (Evans et al., 2001). Downward trends in nitrate were observed only in central Europe and at some sites in Scandinavia (Evans et al., 2001; Wright et al., 2001). Similarly Skjelkvale et al. (2001b) noted that only the Central European region of the ICP-Waters network exhibited a significant regional trend in nitrate concentrations. These comparisons suggest that the long-term nitrate declines recorded from five mountainous areas of the CR are exceptional. A surprising decline in the mean nitrate concentration of streams was also observed in the USA. The rate of nitrate decline was -3% per year, or about $-1 \mu\text{eq L}^{-1} \text{yr}^{-1}$, near Mount Moosilauke, New Hampshire between 1973–1974 and 1996–1997 (Goodale et al., 2003) (Fig. 8). The cause of that nitrate concentration decrease was not evident because no significant long-term trend of N in bulk deposition was observed at the nearby intensively monitored Hubbard Brook Experimental Forest. Goodale et al. (2003) suggested that the 10% increase in atmospheric concentrations of CO_2 during the study period probably stimulated vegetation growth, thereby increasing N uptake and reducing stream water N concentrations. In any case this long-term decline of nitrate in New

Hampshire was fairly low in comparison to the decline in the CR (Fig. 8).

4.6. Representativeness of repeated regional surveys

Our discussion compares water quality trends derived from two different methods. Our trends were derived from two surveys 10 yr apart at 148 sites in western Bohemia and these are compared to trends from long-term monitoring studies at individual sites outside of the CR (with monthly or annual sampling) spanning various periods. Direct comparisons using the same methodology could not be made because the authors are not aware of repeated regional surveys outside of the CR. The limitations of inferring trends from two sample points in time are a legitimate concern. However, our results for the major solutes are similar to the regional results of Vesely et al. (2002a) from four other Czech mountain ranges, especially with respect to nitrate (Fig. 8). The marked environmental changes that occurred in the CR between the two surveys ensured that even a relatively limited number (hundreds) of samples can show significant differences. Thus the repeated survey in the Slavkov Forest objectively documented the chemical recovery of stream waters.

Stream waters should have higher temporal variability and should respond more quickly to environmental changes than lake waters because of generally shorter water residence times. Thus streams should recover more rapidly from acidification and comparison of recovery in lakes and streams (Figs. 7 and 8) should be made with caution.

It is somewhat risky to extrapolate long-term site-specific data to the regional level (Stoddard et al., 1998). However, Likens (1999) reported that long-term patterns of calcium and sulfate concentrations and fluxes in stream water were similar for a small reference catchment W6 (0.13 km^2) at Hubbard Brook, New Hampshire, USA and the whole Hubbard Brook valley (32 km^2). Such similarity in response to acidic deposition over more than two orders of magnitude in catchment area is important for the interpretation of results from different landscape scales (Likens, 1999). The regional trends from the Slavkov Forest surveys can be compared to the long-term trends from the Lysina and Pluhuv Bor catchments, which have temporally frequent (usually weekly) sampling that spans the period of our two regional surveys. Comparing the 0.27-km^2 Lysina catchment (Hruska et al., 2002) with the 820-km^2 regional survey of the Slavkov Forest (this study) likewise shows surprisingly similar patterns for sulfate (Fig. 7), calcium and magnesium (SO_4 : $-28 \mu\text{eq L}^{-1} \text{yr}^{-1}$, Ca: $-11 \mu\text{eq L}^{-1} \text{yr}^{-1}$, Mg: $-3 \mu\text{eq L}^{-1} \text{yr}^{-1}$ at Lysina (Kram et al., 2002); SO_4 : $-30 \mu\text{eq L}^{-1} \text{yr}^{-1}$, Ca: $-12 \mu\text{eq L}^{-1} \text{yr}^{-1}$, Mg: $-5 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the

Slavkov Forest surveys). The Pluhův Bor catchment (area 0.22 km²; Krám et al., 1997; Shanley et al., 2004) exhibited the most rapid sulfate decrease of $-50 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the 1990s (Krám et al., 2002; Hruška and Krám, 2003) and a decrease of divalent base cations of $-15 \mu\text{eq L}^{-1} \text{yr}^{-1}$. The agreement of our trends from those of the individual long-term monitoring sites supports the representativeness of the regional surveys in the Slavkov Forest.

5. Conclusions

The decrease of sulfate and nitrate concentrations in stream waters of the Slavkov Forest in the 1990s was extreme and unprecedented even in comparison to other areas that experienced significant recovery, including other mountainous areas of the CR, southern Scandinavia, and southwestern Ontario. Decreases of SAA, SBC and ANC were heterogeneous and related to the original stream water pH.

The change of surface water pH depended on the initial pH, similar to other areas of the CR and Canada. The pH increased markedly in waters that were strongly acidic at the beginning of the 1990s. This increase was generated by a significantly greater decrease of SAA relative to SBC in streams. On the other hand, pH unexpectedly decreased in waters with an initial slightly alkaline pH because the mean decrease of SBC concentration was greater than the corresponding decrease of SAA. SAA were probably more influenced than SBC by changes in atmospheric deposition fluxes. On the other hand SBC was probably more influenced by leaching from soils and vegetation. A marked increase of pH in precipitation and particularly through-fall was observed in the Slavkov Forest. These higher pH inputs resulted in less leaching of SBC from foliage and soils, especially in catchments with slightly alkaline drainage water pH. As a result, SBC decreased more rapidly than SAA in these high-pH streams, and pH of stream water decreased.

Acknowledgements

This project was funded by the Grant Agency of the Czech Republic (grant No. 205/01/1426) as well as the Czech Geological Survey. We appreciate fruitful cooperation of Jakub Hruška and Josef Veselý. Valuable comments by Douglas A. Burns, Norman E. Peters and the four anonymous reviewers are greatly appreciated.

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