# Meteorological Situations in 2007 and their Implications for the Cycling of Selected Chemical Elements in a Central Bohemian Forested Catchment

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**Abstract**: Comparison of the annual bulk precipitation in the Lesní potok experimental catchment (Central Bohemia, Czech Republic) in the hydrological year 2007 (758.8 mm) with the average annual value between the years 1995 and 2006 (737.4 mm) indicates almost similar values, whereas the stream water discharge in 2007 amounts to only 38.2% of the average annual value of the comparable time span. It has been found that the low discharge in 2007 resulted from the extremely temperate winter and from the anomalous distribution of the precipitation events throughout the year. These factors, together with higher pH values of stream water in 2007, reduced the output of elements from the catchment. The output of dissolved Al, Be, Cd, Mn, Ni, Pb, and Zn through the stream water in 2007 is amounted to only 15 to 20% of their annual output in 1995–2006. The unusually low output of the elements distinctly affected their budgets in the catchment changing towards more positive mass balance values. This holds especially for the major base cations Ca, Mg, and Na (e.g. shift from –1460 to –127 mg/m$^2$year for Ca and from –572 to +15 mg/m$^2$year for Mg) and also for the trace elements Be, Mn, Ni, and Sr (e.g. shift from –368 to +144 μg/m$^2$year for Be, from 2820 to 14 300 μg per m$^2$year for Mn, and from 191 to 7 790 μg/m$^2$year for Sr). The meteorological conditions in 2007 induced, to a certain extent, the recovery of the acid-sensitive ecosystem disturbed by a long-term high input of acid precipitation.

**Keywords**: precipitation; forested catchment; elements; mass balances

The massive input of anthropogenic atmospheric acidifiers, in the form of "acid rain", culminated in the Central Europe in the 2nd part of the 20th century. It strongly affected the mobility of numerous elements in ecosystems and caused the degradation of vulnerable soils covering the acid-sensitive bedrocks (Likens *et al.* 1996). The unfavourable situation has been changing since the 90's of the last century, when the quality of atmospheric deposition started to improve (Skřivan *et al.* 2000b; Hruška *et al.* 2002; Navrátil *et al.* 2005). Between 1995 and 2007, this could be illustrated

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by one half and almost two thirds decrease of $H^+$ and $SO_x$ depositions, respectively, in the Lesní potok (LP) catchment in Central Bohemia (unpublished data).

In 2007, the evolution of the precipitation events in Central Bohemia was atypical in several aspects, which include (*i*) a considerably low stream water discharge and (*ii*) increased values of stream water pH in the LP catchment. These factors resulted in extremely low outputs of the studied elements from the catchment.

The objective of the present study was to determine and compare the mass balance of the elements in the hydrological year 2007 with a long-term period (1995–2006) in the LP catchment. In order to determine the influence of weather on the mass balance of water and several elements, the evolution of different types of synoptic situations in 2007 is discussed.

### Site description

The LP catchment is situated approx. 30 km ESE from Prague, in the Nature State Reserve "Voděradské bučiny" (The Voděrady Beechlands), Central Bohemia (Figure 1). The catchment area (0.765 $km^2$) is underlaid by granites of the Central Bohemian Pluton. The closing profile is at 406 m a.s.l., and the highest (southern) point of the catchment is at 505 m a.s.l. 99% of the catchment area are forested; 46% with coniferous (mainly Norway spruce; *Picea abies* L. Karst) and 53% with deciduous (mainly European beech; *Fagus sylvatica* L.) trees.

The average annual temperature is 9°C (Navrátil *et al.* 2003). The coldest month is January with the mean temperature +0.2°C, the warmest is June, with +14.1°C (Skřivan *et al.* 2000b; Navrátil *et al.* 2004). High evapotranspiration (~80%) results from almost total afforestation of the area and from relatively high summer temperatures (Navrátil *et al.* 2003).

## MATERIALS AND METHODS

The monitoring of the atmospheric depositions and stream water discharge in LP catchment started in 1989; however, the complete data for the input and output fluxes of elements are available since 1995. Consequently, for the comparison of the long-term mean fluxes with those in 2007, we used the data from the monitoring period taken between 1995 and 2006. The values of the monthly temperatures were provided by the meteorological station Ondřejov (546 m a.s.l.), the Czech Hydrometeorological Institute. The Ondřejov observatory is located near the LP catchment and is not influenced by Prague agglomeration.

The samples of the bulk precipitation were collected in monthly periods at the Tree breeding station Truba (TR), field site of the Faculty of Forestry and Wood Sciences, the Czech University of Life Sciences, approx. 5.5 km NE from the catchment. Samples of the beech and spruce throughfall (LP 6 and LP 7, respectively) were collected near the weir of the catchment (Figure 1). The methods of precipitation sampling and treatment were described in detail in Skřivan *et al.* (2000a).

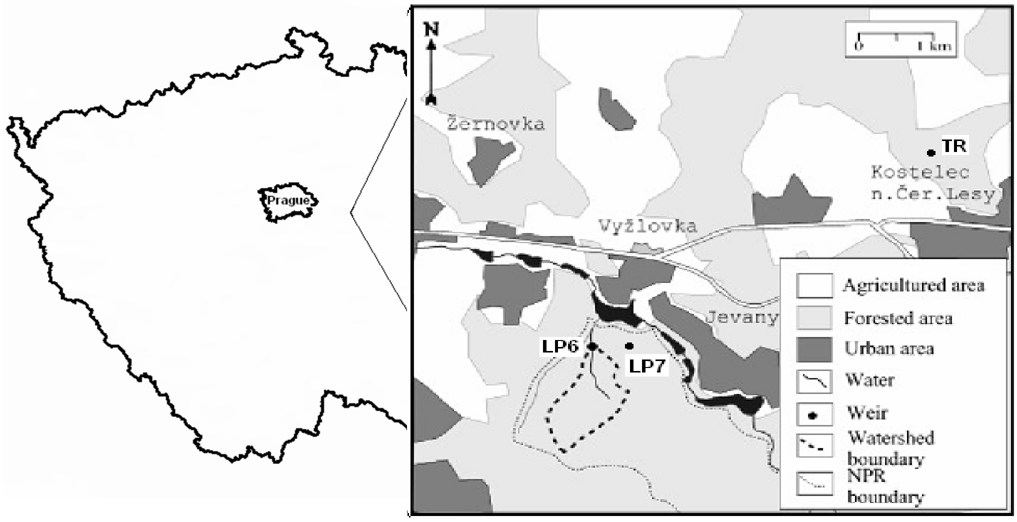

Figure 1. Location of the Lesní potok catchment in the Czech Republic

Table 1. Ratio of monthly precipitation with respect to its annual amount (%)

| Month | XI | XII | I | II | III | IV | V | VI | VII | VIII | IX | X |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 5 | 6 | 7 | 7 | 8 | 5 | 10 | 12 | 14 | 12 | 8 | 6 |
| 2007 | 5 | 4 | 13 | 5 | 6 | 0 | 10 | 16 | 11 | 5 | 20 | 5 |

The samples of the stream water were collected monthly at the Thomson weir of the catchment. The weir is equipped with a digital limnigraph. The groundwater was collected from the depth of 4.2 m (approx. 2 m below the groundwater level) in a borehole (sealed with inert material) near the weir, after complete exhaustion of the stagnant water.

The collected samples of the precipitation and stream water were analysed in the laboratories of the Institute of Geology AS CR. The samples were analysed with AAS (Varian SpectrAA 300, using flame technique and graphite furnace GFAAS), and with ICP-OES (Thermo Elemental, Intrepid Duo) with axial plasma and ultrasonic CETAC nebuliser (model U-5000AT+). If necessary, the samples were pre-concentrated by evaporation in quartz 2 L bulb, using the vacuum evaporiser Büchi Rotavapor B-200.

The mass balances of the elements studied were determined on the basis of the input fluxes (through weathering and atmospheric deposition) and the output fluxes (through stream water and groundwater discharges). The weathering fluxes of the elements were calculated by using their mean concentrations in the bedrock of the LP catchment and the chemical weathering rate of the bedrock (Navrátil *et al.* 2007). The major mineral sources of the elements studied were aluminosilicates (K-feldspar, plagioclase, biotite and muscovite) that have approximately the same orders of the dissolution rate. This fact allowed to make an independent estimation of the weathering fluxes of the elements studied using Na weathering flux as the indicator of the whole-rock weathering (Drever & Clow 1995; Navrátil *et al.* 2007). The input of the elements into the system by weathering was considered to be constant within the examined time span (1995 to 2007). The annual fluxes of the elements in the bulk precipitation sampled at the locality TR were used as the primary information of their atmospheric inputs. To estimate the total deposition of the elements, involving complete wet and dry deposition, we used the data normalised by the ratio of Na in the mean throughfall and in the bulk precipitation, according to the method of Bredemeier (1988). The annual output of the elements through the stream water discharge was estimated as the sum of their daily output fluxes calculated from their concentrations in the monthly collected samples and water discharge derived from the current limnigraph measurements. The amount of the annual groundwater runoff was calculated from the chloride budget (Navrátil *et al.* 2003, 2007). It corresponds to approx. 10% of the annual stream water runoffs in 1999 and 2000. The analyses of the groundwater samples collected monthly over the years demonstrated that the concentrations of the ele-

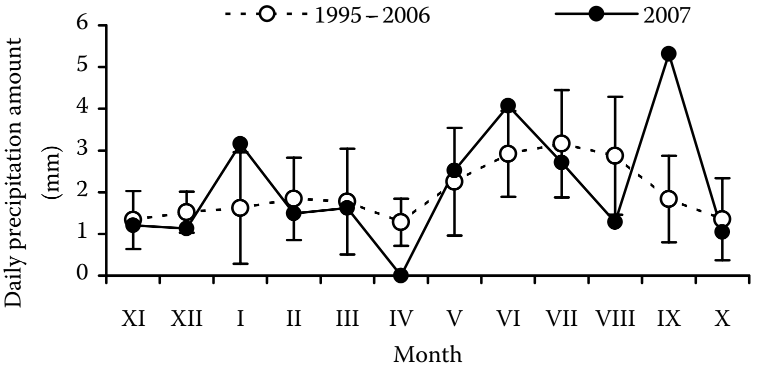

Figure 2. The daily precipitation amounts (mm) in 2007 and in the period 1995–2006; the daily average was calculated from the corresponding monthly values, vertical lines depict the standard deviation

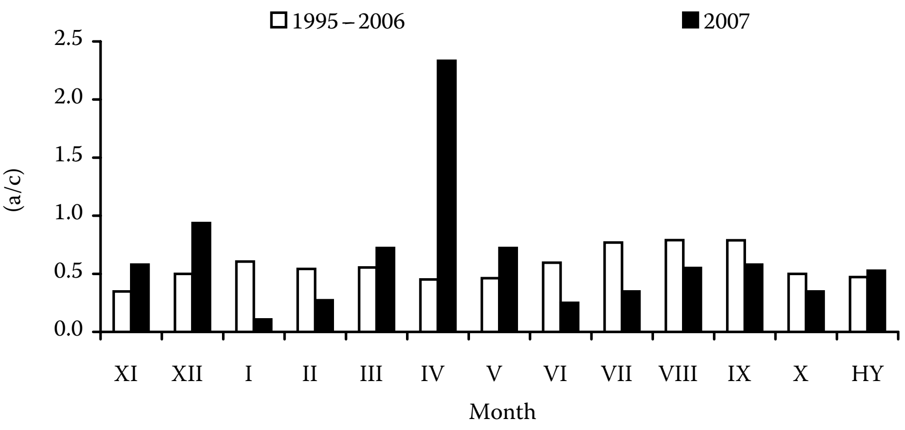

Figure 3. Ratio of the occurrence of the cyclonal and anticyclonal synoptic situations; a – number of days with anticyclonal synoptic situation; c – number of days with cyclonal synoptic situation; HY – mean values for the hydrological year 2007

ments studied remained almost constant, with oscillations less than 20% rel.

## RESULTS AND DISCUSSION

### Precipitation

The annual precipitation in the hydrological year 2007 (758.8 mm) resembled the annual value from 1995 to 2006 (735.7 mm). The highest monthly precipitation (Table 1) was observed in the summer season, mainly in July (14% of the annual amount), whereas the lowest precipitations (approx. 5%) occurred in November and April.

While the total annual values of precipitation in the period 1995–2006 and in 2007 were almost similar, the distribution of the monthly precipitation in 2007 differed in the course of the long-term period. The beginning of the hydrological year 2007 corresponded to the long-term precipitation values, but the value was almost two-fold higher in January (Figure 2). Since February 2007, the precipitation was lower compared to the long-term average, and in April 2007 it was almost negligible (mere 2 mm). The period between May and July 2007 corresponded to the long-term average values; the precipitation in August 2007 was extremely low (5% in 2007 compared to the long-term 12% of the annual amounts). The precipitation in the cold period of 2007 was high; in September it was even the highest in the whole hydrological year (Figure 2).

The extremely low precipitation amount in April resulted probably from a higher occurrence of anticyclonal situations in spring 2007 (Figure 3) that act against the rise of precipitation in the cold period of the year. On the contrary, the anticyclonal situations can support the occurrence of local precipitation events and storms in warmers period of the year. Thus their occurrence in the warmer May of 2007 caused the

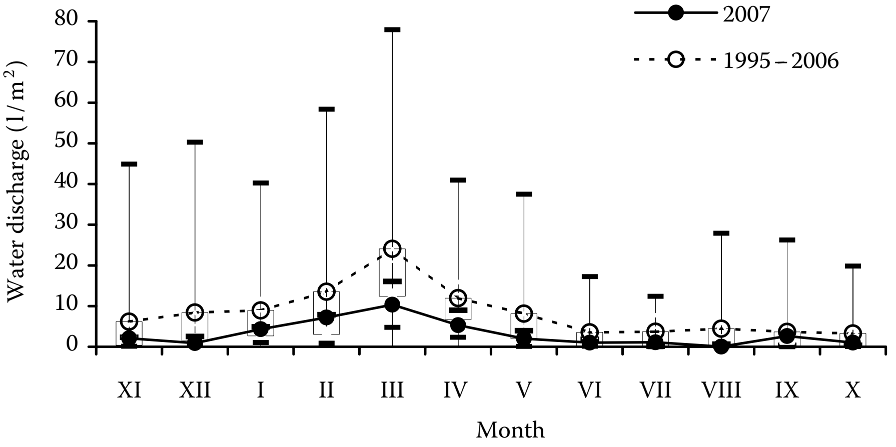

Figure 4. Mean water discharge amount through the years 1995 and 2006 compared to the discharge in 2007

Table 2. Outputs of selected elements from the catchment through surface discharge (mg/m$^2$/year) (Φ pH – average pH values)

| Year | Φ pH units | Discharge (l/m$^2$/year) | Al | As | Ba | Be | Cd | Fe | Mn | Ni | Pb | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1995 | 4.72 | 124.17 | 143 000 | 215.0 |  | 1 170 | 73.8 | 10 400 | 32 300 |  | 32.90 |  | 3 000 |
| 1996 | 4.77 | 144.66 | 162 000 | 103.0 |  | 1 420 | 72.4 | 15 000 | 39 500 |  | 81.90 | 29 800 | 3 130 |
| 1997 | 4.88 | 94.70 | 90 400 | 73.6 |  | 575 | 28.9 | 14 300 | 19 900 |  | 23.70 | 13 600 | 1 840 |
| 1998 | 5.13 | 23.68 | 14 600 | 10.8 |  | 99.2 | 4.7 | 4 670 | 3 670 |  | 6.86 | 2 990 | 277 |
| 1999 | 4.95 | 93.89 | 70 100 | 25.8 |  | 425 | 28.2 | 8 230 | 12 400 | 593 | 23.50 | 12 500 | 1 900 |
| 2000 | 4.87 | 103.53 | 59 200 | 18.6 | 3 130 | 477 | 26.1 | 11 700 | 13 600 | 534 | 2.71 | 11 400 | 1 350 |
| 2001 | 4.88 | 50.56 | 39 000 | 9.3 | 1 740 | 261 | 13.6 | 9 500 | 7 010 | 357 | 12.60 | 6 240 | 1 070 |
| 2002 | 4.83 | 205.71 | 165 000 | 79.2 | 7 960 | 1 250 | 60.4 | 43 700 | 71 300 | 1 750 | 10.50 | 28 000 | 4 630 |
| 2003 | 4.93 | 147.63 | 101 000 | 16.8 | 5 030 | 812 | 39.5 | 24 200 | 39 000 | 1 040 | 3.12 | 16 500 | 1 860 |
| 2004 | 4.94 | 48.41 | 38 000 | 10.2 | 1 090 | 211 | 11.5 | 3 310 | 4 120 | 263 | 4.67 | 5 220 | 346 |
| 2005 | 4.93 | 63.32 | 44 800 | 11.9 | 2 670 | 283 | 14.2 | 7 680 | 5 090 | 342 | 2.72 | 6 440 | 919 |
| 2006 | 5.18 | 95.73 | 64 300 | 31.8 | 3 290 | 470 | 24.2 | 11 400 | 13 600 | 373 | 3.71 | 7 090 | 1 650 |
| Mean | 4.94 | 99.67 | 82 600 | 50.5 | 3 600 | 670 | 33.1 | 13 700 | 21 800 | 656 | 17.40 | 12 700 | 1 830 |
| 2007 | 5.20 | 38.09 | 15 600 | 9.28 | 1 160 | 104 | 4.89 | 9 240 | 3 260 | 118 | 2.46 | 4 760 | 363 |
| % |  | 38.20 | 18.9 | 18.4 | 32.7 | 15.5 | 14.8 | 67.5 | 15.0 | 18.0 | 14.10 | 37.5 | 19.8 |

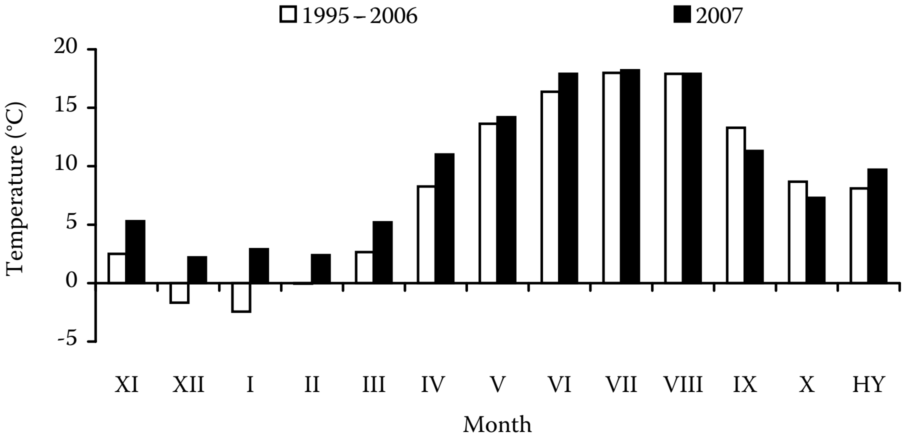

Figure 5. Course of the mean monthly temperatures in the hydrological year 2007 compared to those throughout the long-term average (1995–2006).

enhancement of the monthly precipitation ratio to the standard value by 10%. The cyclonal synoptic situations in 2007 occurred mainly in June and September (Figure 3) and were manifested by high precipitation in comparison with the long-term average precipitation values in these months (Figure 2). The precipitation in July and August 2007, however, was relatively lower, in spite of the occurrence of cyclonal situations. This was caused by the fact that in July only 16 days occurred with the "westerly cyclonal synoptic situation" (Wc) or the "southwestern synoptic situation with southerly trajectory of cyclones" (SWc2) that caused slightly increased precipitation (Křivancová & Vavruška 1997). In August, only 7 days were characterised by the situation "trough of depression over our territory" (B) and by "cyclone over our territory" (C), both situations with the same character (Racko 2007).

### Water discharge

In the period 1995–2006, the water discharge usually increased in the cold months between November and March and culminated during the snowmelt events in March (Figure 4). The following months (frequently up to June) were characterised by a distinctive decrease of the stream water discharge. This was caused by lower precipitation amounts and a higher evapotranspiration. Almost similar monthly discharge between June and October (Figure 4) resulted from the combination of declining precipitation and decreasing evapotranspiration.

The patterns of the discharge trends in 2007 and in the long-term period are similar (Figure 4); however, the overall amount of the water discharge was considerably lower in 2007 (only 38.2% of the average between 1995 and 2006). On the other hand, the sparsity of the individual values of the water discharge throughout the long-term period does not prove any statistical difference.

The main reason that probably affected the extremely low stream water discharge in 2007 was related to the higher air temperatures throughout

Table 3. Average pH values (Φ pH) of surface stream and the discharge from the catchment in a given month between 1995 and 2006, and in 2007 (in l/m$^2$)

| Month | Φ pH | Discharge | Φ pH | Discharge |
|---|---|---|---|---|
| | 1995–2006 | | 2007 | |
| XI | 4.92 | 6.16 | 6.02 | 2.08 |
| XII | 4.89 | 8.40 | 5.55 | 0.91 |
| I | 4.87 | 8.94 | 5.03 | 4.33 |
| II | 4.87 | 13.53 | 5.10 | 7.20 |
| III | 4.92 | 24.08 | 5.36 | 10.33 |
| IV | 4.87 | 11.97 | 5.78 | 5.32 |
| V | 4.82 | 8.14 | 5.92 | 2.00 |
| VI | 4.78 | 3.53 | 5.77 | 1.02 |
| VII | 4.80 | 3.68 | 6.40 | 1.10 |
| VIII | 4.70 | 4.45 | 6.67 | 0.02 |
| IX | 4.88 | 3.65 | 5.30 | 2.63 |
| X | 5.07 | 3.28 | 5.71 | 1.03 |

the year (Figure 5). In January 2007, the temperature exceeded the long-term value even by 5°C. Generally, the temperatures were significantly higher in the first half of the hydrological year 2007 (since November to April), then the deviations were not significant. High temperatures in the winter months prevented the formation of the frost-bound surface soil layer and that of compact snow layer, so the water discharge in the spring was not affected by the snow melt surface runoff. The entire amount of winter precipitation immediately infiltrated into the saturated zone of the soil.

### Fluxes of elements

The variable distribution of the precipitation events in the hydrological year 2007, a low water discharge and a higher water pH resulted in strongly decreased outputs of certain elements from the catchment through the stream water discharge (Table 2). This holds especially for the elements with mobility strongly dependent on the pH value of the system.

The pH values of the stream water discharge in all months of 2007 were distinctively higher than the corresponding mean values between 1995 and 2006 (Table 3). This conspicuous difference was caused by the low discharge in 2007, when the soil water persisted for a longer time within the soil solid matter which was therefore better saturated with major base cations coming from weathering and exchange processes (Navrátil 2003; Navrátil *et al.* 2003). Higher pH also reflected the considerably lower input of atmospheric acidifiers, in particular when compared with those in the last years of the 20th century (Skřivan *et al.* 2000b; Fišák *et al.* 2006).

The higher pH of the soil and stream sediments affected the distribution of a number of elements between the solid matter and pore water in all cases in favour of their sequestration in solid matter.

Table 4. Balance of the element inputs and outputs between 1995–2006, compared to those in 2007 (Φ average values)

| Element | Inputs | | | Outputs | | | Net change | |
|---|---|---|---|---|---|---|---|---|
| | total deposition | | Φ rock weathering | stream runoff | | subsurface discharge | Φ 1995–2006 | 2007 |
| | Φ 1995–2006 | 2007 | | Φ 1995–2006 | 2007 | | | |
| **(mg/m$^2$/year)** | | | | | | | | |
| Al | 40.1 | 18.4 | 2503 | 82.7 | 15.6 | 0.17 | 2460 | 2500 |
| Ca | 319 | 228 | 253 | 1840 | 416 | 193 | –1460 | –127 |
| K | 154 | 208 | 1315 | 123 | 37.2 | 16.4 | 1330 | 1470 |
| Mg | 54.3 | 40.4 | 176 | 765 | 164 | 37.4 | –572 | 15 |
| Na | 174 | 117 | 887 | 857 | 255 | 154 | 52 | 596 |
| **(μg/m$^2$/year)** | | | | | | | | |
| As | 602 | 98.4 | 225 | 52.8 | 9.28 | 64.8 | 710 | 249 |
| Ba | 1210 | 947 | 28 800 | 3560 | 1160 | 178 | 26 300 | 28 400 |
| Be | 14.0 | 8.98 | 244 | 621 | 104 | 5.19 | –368 | 144 |
| Cd | 64.2 | 44.3 | 29.0 | 33.1 | 4.89 | 0.15 | 60 | 68 |
| Fe | 41 900 | 22200 | 385 000 | 13 700 | 9240 | 31 900 | 381 000 | 366 000 |
| Mn | 16 400 | 9330 | 12 500 | 21 800 | 3260 | 4260 | 2820 | 14 300 |
| Ni | 228 | 126 | 616 | 656 | 118 | 63.8 | 124 | 560 |
| Pb | 1650 | 531 | 1440 | 5.73 | 2.46 | 0.23 | 3090 | 1970 |
| Sr | 716 | 365 | 12 800 | 12 700 | 4760 | 645 | 191 | 7790 |
| Zn | 7330 | 5020 | 1320 | 1830 | 363 | 44.0 | 6770 | 5930 |

Lower concentrations of the dissolved Al, Be, Cd, Mn, Ni, Pb, and Zn in the stream water, together with the generally low discharge, resulted in their extremely low outputs through the stream water discharge in 2007 that amounted to only 15–20% of their mean values between 1995 and 2006. The output of As was also considerably lower in 2007; in this case due to the high As deposition and output fluxes throughout the early years of the compared time period.

### Element budgets

Since the beginning of the industrial revolution throughout the era of increased deposition of anthropogenic acidifiers, the element budgets of numerous elements in soils have been seriously disturbed. This holds especially for the soils evolved on acidic bedrock, where the leaching of major base cations has led to depletion of nutrients and numerous trace elements essential for the successful vegetation growth (Likens *et al.* 1996). The recovery of ecosystems is expected after a considerably decreased input of atmospheric acidifiers, when the output of base cations through the water discharge will be at least balanced by their inputs through bedrock weathering and atmospheric precipitation. In present days, the input of atmospheric acidifiers is generally still too high and the degradation of soils continues. Nevertheless, under distinct conditions, the input and output fluxes of base cations and other acid-sensitive elements could be balanced already at present, as indicated by the results of the mass balance of elements in the hydrological year 2007 (Table 4).

The estimation uncertainty of the mass balance data from the input and output fluxes is related to many factors. Several main factors are discussed below. Certain inaccuracies of the estimation of output through the stream water discharge may be related to the scarce information concerning the chemistry of dominant hydrologic events (spring snowmelt and summer torrents), resulting from monthly periods of sampling and analysing the stream water. Navrátil *et al.* (2007), however, found that these should not significantly affect Mn mass balance in the LP. Additional quantities of the elements are exported from the catchment through the groundwater discharge in the hyporheic zone. The groundwater pH in the LP catchment is approx. by 2 std. units higher than that of stream water, which results in decreased concentrations of elements whose mobility is strongly pH – dependent (acid sensitive elements), such as Al, Be, Cd, Pb, and Zn. On the other hand, Fe, Mn, and As are present in groundwater in greatly increased concentrations, resulting from the balance transformations (followed by changes in solubility and sorption properties) of these elements. Due to the lack of information concerning the groundwater runoff in 2007, we applied the value of the groundwater runoff as calculated by Navrátil *et al.* (2003) in the mass balance calculations for the entire time span discussed (1995 to 2007). It is evident that the values of groundwater output of elements in 2007 used for the mass balance calculations are overestimated (due to the positive dependence of the ground water and stream water runoff).

In spite of the mentioned overestimation of the element outputs in the mass balance calculations, the data summarised in Table 4 clearly show that the outputs of the most mobile elements Be, Ca, Cd, Mg, Ni, and Sr in 2007 were considerably lower, with crucial role of the low stream water discharge and increased pH of stream water on the element budget in that year. The budgets of Ca and Mg seem almost balanced in 2007, but if we consider their extensive incorporation into organic matter through the biological uptake (and wood harvesting), then these two essential elements will be deficient again. The accumulation of the less mobile elements (Al, As, Ba, Fe, Pb, Zn) continues in spite of the considerably lower atmospheric (anthropogenic) inputs of As, Pb, and Zn. The outputs of As and Fe (and, to a lesser extent, of Mn) through the ground water discharge are always high due to their high concentrations at slightly reducing conditions of groundwater, but their mass budget was surplus in 2007. Considering the biological uptake of major nutrients and several essential elements (mainly K, Mn, Mg, Ca) by forest trees and their gradual harvesting, then the real mass balance of these elements should be by far less positive.

## CONCLUSIONS

The study provides the geodynamics of selected chemical elements at the forested Lesní potok experimental catchment in the anomalous year 2007. The meteorological, hydrological and mass balance data of the hydrological year 2007 are compared with the corresponding numbers for the period between 1995 and 2006. The conclusions are as follows.

### Impact of the anomalous meteorological situation in 2007

The anomalous meteorological situations in 2007 affected the distribution of the precipitation events throughout the hydrological year. The occurrence of the anticyclone situations in the warmer period probably supported the limited occurrence of local precipitation events. The enhanced precipitation was evoked by the cyclonal synoptic situations, their occurrence was however limited in 2007. Among other affecting factors, the mild winter and lack of the snow layer could contribute to the low water discharge throughout the year 2007 (it amounted to only 38.2 % of the long-term average).

### Element budgets

The higher pH values of the stream water in 2007 (volume weighted mean 5.20 compared to the long-term 4.94) resulted from the longer residence time of pore water (assumed from low precipitation and its distribution throughout the year) and decreased input of atmospheric acidifiers. These factors affected the mass budget of numerous pH sensitive elements towards more positive values: (i) they considerably reduced the depletion of base cations Ca, Mg, and trace element Be, and (ii) significantly increased the accumulation of Mn, Na, Ni, and Sr.

The anomalous evolution of synoptic situations and climatic conditions in 2007 considerably affected the mass balance of many elements in the monitored forested catchment. The described circumstances in that year induced favourable conditions that tended to the recovery of the formerly disturbed acid-sensitive ecosystem.

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