The role of groundwater in the acidification of the hydrosphere – examples from small catchments in the Bohemian Massif

ZBYNEK HRKAL, JOSEF BUCHTELE, EEVA TIKKANEN, ASKO KÄPAHO & JAROMIR SANTRUCEK

Hrkal, Z., Buchtele, J., Tikkanen, E., Käpyaho, A. & Santrucek, J. 2002: The role of groundwater in the acidification of the hydrosphere - examples from small catchments in the Bohemian Massif. *Norges geologiske undersøkelse Bulletin 439*, 99-105.

The aim of the presented study was to assess the impact of the groundwater on the degree of acidification of surface waters in small catchments. Quantitative hydrogeological analysis based on the results of the SACRAMENTO hydrological model was aimed at the assessment of the contribution of baseflow representing the groundwater discharge in the total runoff. Comparison of single pH measurements in surface water with the corresponding actual and modelled water discharge was used as the information in the quantitative part of the data processing. The obtained results showed different protective powers of the aquifers against acidification, a conspicuous decrease in the soil buffer capacity of the Krusné hory Mts. and a significant influence of throughfall precipitations on the groundwater quality.

Zbynek Hrkal, Josef Buchtele, Jaromír Santrucek, Charles University, Dept. of Hydrogeology, Czech Republic.
Eeva Tikkanen, Asko Käpyaho, University of Helsinki, Finland.

Introduction

The Czech Republic is one of several countries where the effects of anthrogenic atmospheric acidification first began to reveal themselves in the early 1960s. However, the mass extinction of forest vegetation, first in the higher parts of the Krusné hory Mts. and later in the Jizerské hory and Krkonose Mts., demonstrated the true extent of acidification. This provided conclusive evidence of the widespread nature of the acidification, but some doubts still prevailed about the degree of acidification of groundwaters. Some regional studies (Hrkal 1992, Hrkal & Fottová 1999) reported evidence of progressive acidification of shallow, near-surface aquifers in the crystalline bedrock complexes which revealed a considerable decrease in alkalinity leading to the complete disappearance of bicarbonates, decrease in pH, and an increase in Al and Be concentrations. Whilst the quality of surface waters is affected by atmospheric deposition directly and immediately, the impact of rainfall on the chemical composition of groundwaters is delayed. Owing to the contact of groundwater with the bedrock environment, and also primarily with soil strata, the groundwater enjoys a degree of potential buffering against acidification, and consequently may play an important role in the resulting chemistry of surface water discharge. However, the proportion of groundwater in the total discharge varies considerably in the course of the year, and consequently a similar variation can be seen in the degree of its impact on the final chemical composition of surface waters.

More precise data on the relationship between the quality of surface water and groundwater could have been obtained only from the monitoring of small experimental catchments. However, in small catchments in the Czech Republic, as in other countries, the contribution of groundwater discharge and quality to surface water was mostly neglected. Comparisons were made between the amount and quality of precipitation on the one hand, and the same for runoff on the other hand, without considering the variability of the groundwater component in the surface water. In recent years, an investigation has been sponsored by Grant 11310005 of the Ministry of Education of the Czech Republic 'Material and energy flows in the upper parts of the Earth', and this has been carried out within the 5th Framework Programme sponsored by the European Union. The LOWRGREP project 'Landscape-use optimisation with regard to groundwater resources protection in mountain hardrock areas' was intended to assess the contribution of groundwater impact on the degree of acidification of surface waters.

Method of data processing

The selection of test sites was the first step of the work. For this reason, data from the experimental small catchment network GEOMON (Fottová 2000) have been used. The degree of acidification in single catchments is controlled by groundwater to a varying extent. The comparison of pH input, represented by atmospheric precipitation and throughfall, and the output, represented by pH and alkalinity of surface runoff, was used to assess the degree of resis-

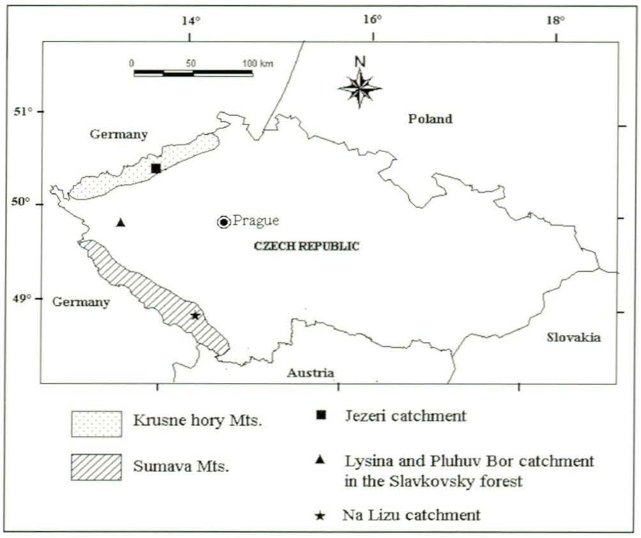

Fig. 1. Location of the test sites.

tivity of individual catchments against acid atmospheric deposition. It was found that the greater the difference between the pH of atmospheric water and in runoff and a higher alkalinity in surface water, the greater was the buffering capacity of the hydrogeological environment and consequently its resistance against acid deposition.

However, the basic information concerning the quality of groundwaters was still missing when assessing the degree of groundwater impact on the final chemistry of surface water. Monitoring of the groundwater quality within the LOWRGREP project commenced in two small catchments (Jezeri and Na Lizu, see Fig. 1) as late as in the beginning of the year 2001. The first results from these localities revealed that the groundwater has a more alkaline reaction that the surface water and, consequently, the groundwater should restrain the impact of 'acid flash floods' on the pH of surface waters. On the other hand, it is obvious that the chemistry of groundwater depends closely on the type of host rock environment. In other words, the pH of groundwater confined to granite will differ from that, for example, in serpentinite. Therefore, the chemical composition of surface water does not depend only on the quantitative parameter, i.e. the proportion of groundwater in the total runoff, but also on the quality of the groundwater.

The work was carried out in two main stages; firstly, a qualitative assessment, which in turn provided data for a quantitative analysis. The quantitative hydrogeological analysis was aimed at an assessment of the contribution of baseflow, representing the groundwater discharge in the total runoff.

The first estimate of quantity of the baseflow is derived from Castany's method (Castany et al. 1970). This calculates the long-term, groundwater runoff assessment in two steps. First, the arithmetic average from a 30-day period of minimum total runoff in each hydrological year expresses the lowest year's runoff. Then, the long-term groundwater assessment is based on the median from these arithmetic averages. Castany et al. (1970) are of the opinion that reliable results can be obtained from a series of measurements over a minimum of 10 years, whereas currently the longest period of monitoring extends only over 5 years. Consequently, the presented results should be viewed with some caution.

To incorporate a more precise baseflow assessment, the SACRAMENTO soil moisture accounting model has been used (Burnash 1995). This model, in combination with the Anderson snow model (Anderson 1973), enables continuous simulations to be carried out over a period of several years. For simulations of the annual rainfall-runoff process, the daily time series are usually used. This is a conceptual water balance model with lumped inputs, with the possibility for its implementation in a semidistributed mode.

There are altogether six runoff components generated by the model:

- DIR – direct runoff, from those parts of the basin which become impervious after saturation,
- IMP – the runoff from the permanently impervious part of basin,
- SUR – surface runoff,
- IN – interflow,
- SUP – supplementary baseflow, i.e., essentially the seasonal component of baseflows,
- PRM – primary baseflow, i.e., the long term part of baseflow.

The daily precipitation and temperature data typical for the catchment area have been used as the input data. The model runoff simulation was then calibrated to the measured surface runoff data and the model assessment of the baseflow compared with the minimum runoff data.

The quantitative part of the data processing was followed by analysis of the groundwater impact on the final chemical composition of the surface flow. The following method was used to express the impact of groundwater on the chemistry of the surface runoff. The hydrogram of the total runoff has been separated into three parts. One part includes the period when the groundwater discharge constitutes at least 50% of the total runoff and when the groundwater chemistry has most effect on the quality of surface waters. The opposite case is represented by a period when the contribution of groundwater discharge in total runoff decreased below 25%. In such a case, the quality of atmospheric water plays a decisive role in the quality of the total runoff. The period during which the contribution of groundwater discharge in total runoff varied between 25 and 50% was considered a mixed period in which none of the explored parameters plays a decisive role. Comparison of single pH measurements in surface water with the corresponding actual water discharge was used as the initial information in the data processing. Seasonal variations in the pH of atmospheric waters expressed as monthly averages were treated separately.

Selection of test sites from GEOMON small catchment network

The process of acidification in the Czech Republic has been monitored in 44 small catchments of the GEOMON system (Fig. 1). Each of these catchments represents a different geological, morphological or vegetation type. They also differ from each other in the intensity of impacts of atmospheric deposition. The method of data collection and assessment of the hydrochemical budget and element flow corresponds with international standards, and the results achieved are therefore comparable with localities abroad.

As follows from Table 1, all studied catchments are affected by acid atmospheric deposition. The average pH of atmospheric precipitation was always below 5, independent of the position of the locality. The long-term arithmetic means of pH in throughfall are always lower than those for precipitation at the same locality. The differences between the pH of precipitation and throughfall are at their highest in the vicinity of the sources of the pollution.

As follows from this five-year monitoring and collection of data, the nature of the geology causes various resistance to acidification. The difference between pH of atmospheric precipitation or throughfall and pH of surface runoff was used as a parameter expressing the degree of buffering against acidification. Using this parameter, the studied catchments can be divided into different groups characteristic of low, medium or high resistance (Table 1).

Table 1. Resistance of individual catchments within the GEOMON network to acidification expressed as a relationship between the pH of rainfall and pH of runoff.

	geology	average pH (precipitation)	average pH throughfall	average pH runoff	difference between pH runoff - pH throughfall	difference between pH runoff - pH precipitation	resistance against acidification
Lysina	granite	4.66	4.26	4.14	-0.12	-0.52	low
Loukov	granite	4.62	4.85	5.14	0.29	0.52	
U dvou loucek	paragneiss	4.16	4.06	4.8	0.74	0.64	
Uhlírská	granite	4.4	3.8	5.18	1.38	0.78	
Lesní potok	granulite	4.49	4.08	5.53	1.45	1.04	medium
Jezeri	paragneiss	4.64	3.65	5.76	2.11	1.12	
Spalenec	granulite	4.81	4.21	6.03	1.82	1.22	
Modry potok	marble	4.7	4.6	6.28	1.68	1.58	
Cervik	sandstone	4.54	4.15	6.12	1.97	1.58	
Polomka	paragneiss amphibolite	4.82	4.36	6.66	2.3	1.84	
Salacova Lhota	paragneiss	4.7	4.68	7.05	2.37	2.35	high
Na Lizu	paragneiss	4.45	4.34	6.72	2.38	2.27	
Anensky potok	gneiss	4.62	4.16	7.05	2.89	2.43	
Pluhuv bor	serpentinite	4.66	4.49	7.33	2.84	2.67	

Two pairs of experimental sites have been selected on the basis of the above-mentioned results. The first is represented by the Jezerí and Na Lizu catchments, characterised by an identical geological background but different intensities of impact of acid deposition. The catchments Lysina and Pluhuv Bor (Kram & Hruska 1994), an example of extreme differences of lithological composition (acid granite at Lysina and ultrabasic serpentinite at Pluhov Bor), represent the second pair of test sites.

Results from selected catchments

The Jezerí and Na Lizu catchments

These two localities were selected in order to provide evidence for the degree of resistance of the geological environment against the prolonged impact of acid atmospheric deposition. It is noteworthy that both catchments are very similar to each other as far as their geology and morphology are concerned. Both lie in mountain areas at altitudes ranging between 475 and 924 m (Jezerí) and 828 to 1024 (Na Lizu) m a.s.l., and both are underlain by Proterozoic metamorphic rocks, paragneisses in particular. However, they differ considerably in the intensity of anthropogenic impact. The Jezerí catchment lies in the Krusné hory Mts and belongs to the so-called 'Black triangle', i.e., the territory of the eastern part of Germany (former GDR), the southwestern part of Poland and the northern part of the Czech Republic, with the highest air pollution in Europe. The Na Lizu catchment is situated in the Sumava Mts. This territory is considered to be one of the cleanest parts of the Czech Republic. Even though the pH values of precipitation on both catchments are very similar, the large difference in throughfall pH values is quite significant.

Comparable geology and morphology are responsible for similar runoff conditions in both catchments. The model determination of baseflow in the Na Lizu catchment (5.2 l/s) corresponds well with the baseflow estimated using Castany's method (4.5 l/s). However, some discrepancy exists between model baseflow estimation (8.0 l/s) and Castany's method assessment (4.5 l/s) in the Jezerí catchment. The specific runoff of groundwater in the Jezerí and Na Lizu catchments is 3.1 l/s/km2 and 5.2 l/s/km2, respectively. No differences exist in the groundwater runoff coefficient (share of groundwater discharge in the total runoff); in the Jezerí catchment this is equal to 42%, whereas in the Na Lizu catchment it amounts to 41%.

There are considerable differences, however, exists in the chemical composition of surface water (Fig. 2). Although the average pH values of atmospheric water from the period 1995-2000 in both catchments are more or less identical (pH 4.5-4.6), the quality of surface water is very different. The pH of the surface runoff in the Na Lizu catchment, c. 7.0, is extraordinarily stable during the course of the year. In the case of the Jezerí catchment, the average pH is one unit lower. A close relationship between the surface water quality and water discharge can be observed in both of these catch-

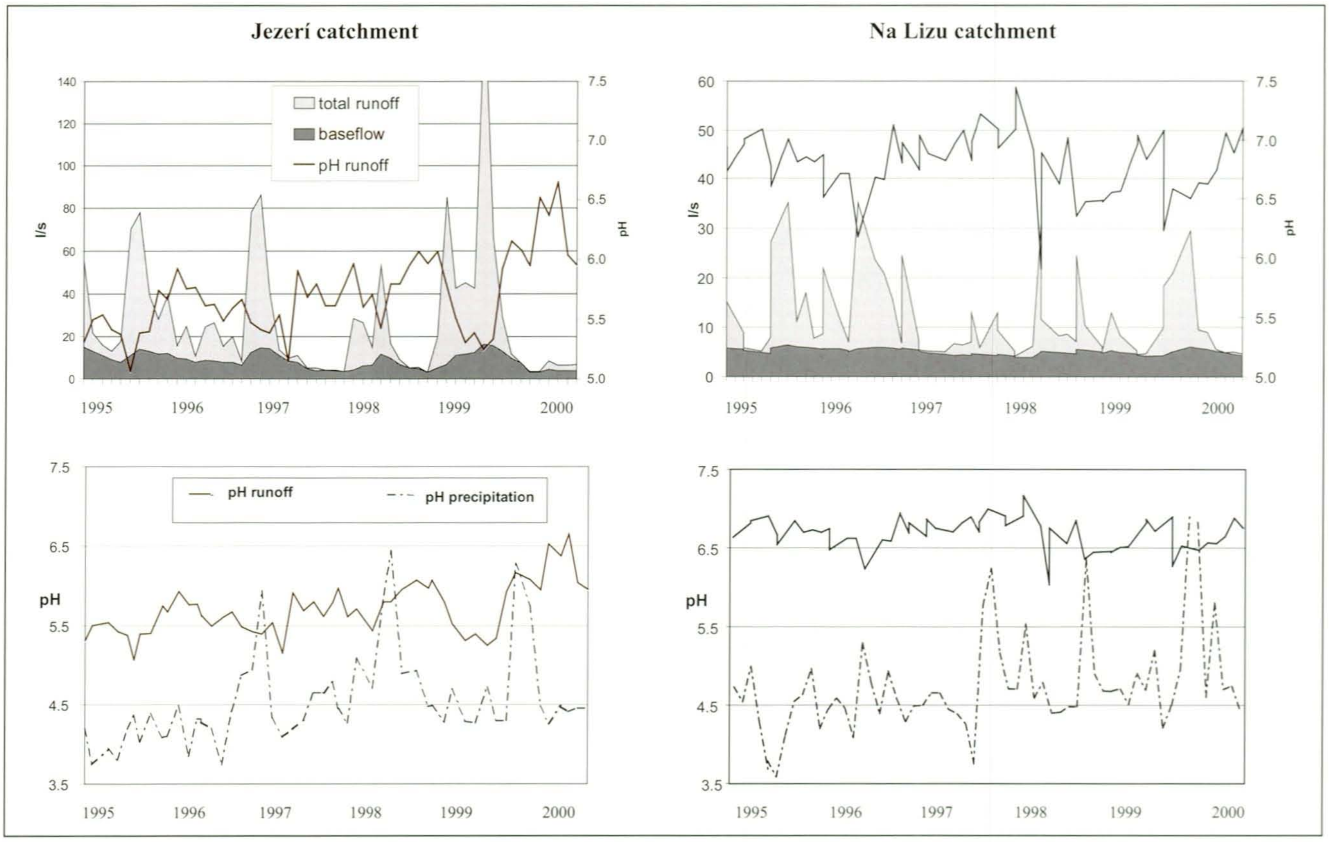

Fig. 2. Relationship between pH runoff and total runoff and baseflow, Jezerí and Na Lizu catchments.

ments. A sharp drop in pH occurs when the proportion of the baseflow decreases. This pH drop is more abrupt at the Jezerí catchment, down to 5.1-5.5, in comparison with values of only 6.0-6.3 at the Na Lizu catchment.

There are two possible solutions to explain these differences:

1. Soils in both catchments are poor in carbonate minerals. If any were originally present, they have long since been dissolved due to the infiltration of acid rain. Aluminosilicates in soil play the main role in the buffering of H+ ions. As their dissolution is controlled kinetically, the best buffering properties of soil are attained during dry periods, i.e., at the time of the highest proportion of groundwater in surface runoff. After torrential rains or snow melting the surface water is more acid, not only for the higher proportion of atmospheric water in surface runoff but also for the shorter time of hydrolysis of soil minerals.

2. Throughfalls have a greater impact on groundwater acidification than precipitations. Acid gases (sulphur and nitrogen oxides, and perhaps also hydrogen fluoride) are to a large extent adsorbed on the needles of conifers and together with dry deposition are washed out by rain and infiltrate into soil. Movement of adsorbed gases and dry deposition is strictly limited and they remain in the vicinity of their sources. Concentrations of H+ ions are ten times higher in throughfall than in precipitations at Jezerí. In spite of the same acidity of precipitation at both catchments, the fast groundwater circulation and slow dissolution of soil minerals cannot fully neutralise the huge amount of acids in the throughfall.

The Pluhuv Bor and Lysina catchments

Both catchments are affected by atmospheric deposition to the same degree. On the other hand, they are markedly different as regards geology and hydrogeology. Both catchments lie in the Slavkovský les upland in western Bohemia (Fig. 1) and are close to each other. Consequently, the climatic and morphological conditions and vegetation are identical in both catchments. The area of each catchment is about 0.2 km^2 and the altitude varies between 800 and 950 m a.s.l. Both catchments are largely covered by spruce forest. The basic difference lies in the bedrock geology. The Lysina catchment occurs exclusively in granite of the Kynzvart Massif, and the local soil has the character of peat gley. The Pluhuv Bor catchment is underlain by serpentinite that is characterised by clayey weathering and very low permeability.

The results of the precipitation/runoff model at the Lysina and Pluhuv Bor localities are less accurate relative to those of the preceding pair of catchments. This fact is demonstrated by the lower degrees of correlation between the measured and the simulated values, which for the Jezeri

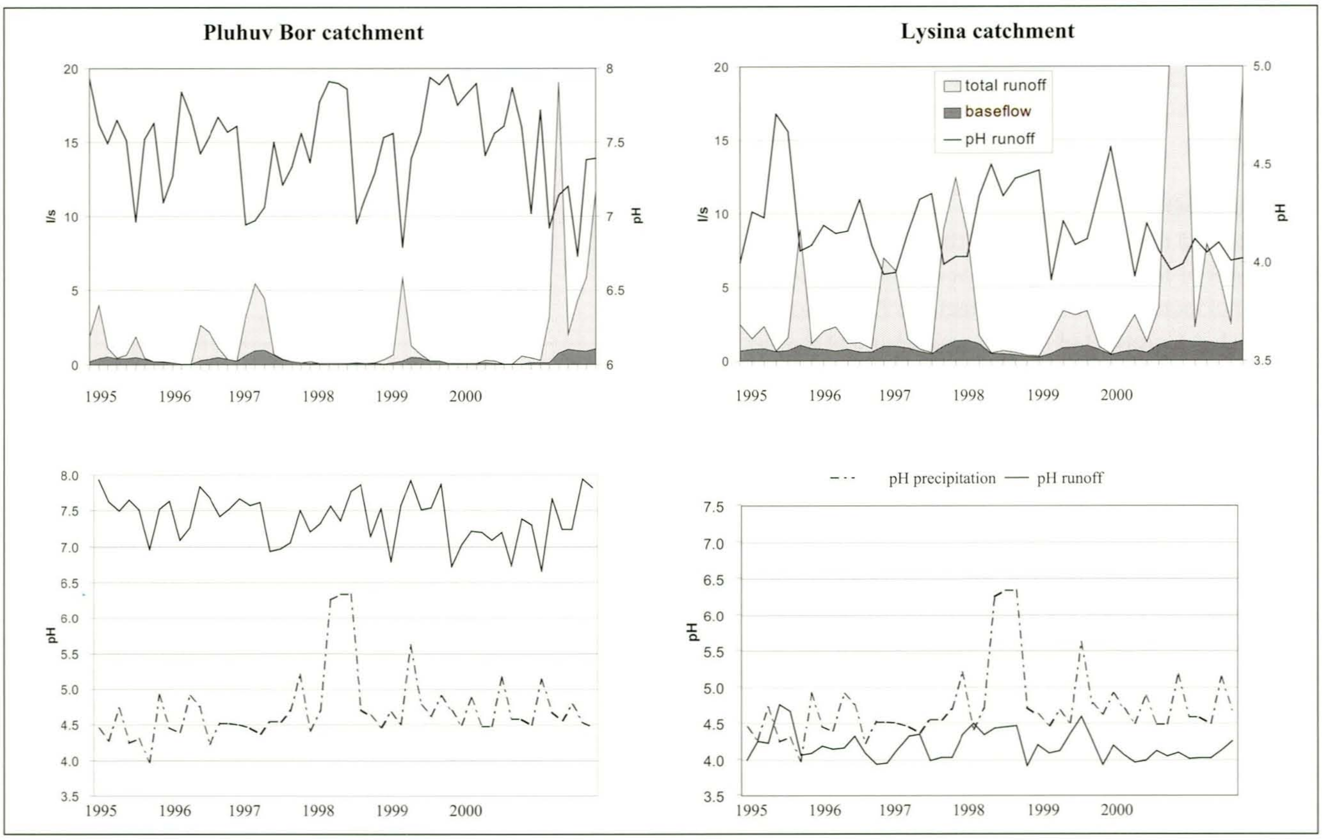

Fig. 3. Relationship between pH runoff and total runoff and baseflow, Pluhuv Bor and Lysina catchments.

and Na Lizu catchments were 0.89 and 0.86, respectively, whereas at the Lysina locality it was only 0.57 and at Pluhuv Bor even less (0.5). The model results suffer from the poor quality of the abundant data on precipitation. These data come from the area of Marianské Lazne, and are not sufficiently representative to characterise the actual precipitation in the model region. However, another analysis and interpretation of the results showed that the accuracy of simulation is sufficient in this case to meet the project objectives.

The low permeability of serpentinite is reflected in the runoff conditions of the Pluhuv Bor catchment. The modelled groundwater discharge constitutes only 19% of the total runoff. The specific discharge of the groundwater is also low, amounting to 1.8 $l/s/km^2$ during the monitored period.

The modelled, specific groundwater runoff in the Lysina catchment (3.3 $l/s/km^2$) including its runoff coefficient (22%) is, due to the completely different geology, greater than that in the Pluhuv Bor catchment. The model determination of baseflow in the Lysina catchment (0.4 l/s) corresponds fairly well with the baseflow estimated using Castany's method (0.7 l/s).

Hydrogeological conditions considerably affect the quality of water drained from both catchments. Although the contribution of groundwater runoff is small with respect to the total runoff, the geochemical character of local rocks at Pluhuv Bor is responsible for a high resistivity against acid deposition. Even though the pH of atmospheric water is only 4.7, the surface water maintains a neutral or slightly alkaline reaction through the whole year. The value of pH of surface water varies between 6.3 and 7.95. The main reason for this is a hydrolysis of basic silicates, e.g. serpentine. Their dissolution is often congruent, much faster than the weathering of acidic rocks, and is able to buffer free H+ ions. Fig. 3 demonstrates a fair relationship between the proportion of groundwater discharge and the total runoff, including pH, in surface water.

The influence of groundwater on the chemistry of discharged surface water is obvious in the Lysina catchment. A similar trend exists here too, i.e., the close relationship between the pH of surface water and the proportion of groundwater runoff in the total runoff. Although the loading of acid atmospheric deposition in the Lysina catchment is similar to that of the Pluhuv Bor catchment, the quality of surface water in the catchments is completely different. The Lysina runoff is the most acidic among all the investigated catchments (Table 1), which is obviously due to the lithology of the soil profile. The groundwater itself in the Lysina catchment is very acid because of humic acids released from the gley horizon rich in peat, and consequently it is not able to neutralise acid rainfall. This fact is particularly evident in periods when the proportion of baseflow and the total runoff exceeds 50%. During this period when the surface water quality is considerably influenced by the chemistry of groundwater, the average pH in the Lysina catchment is equal to 4.3.

Discussion

The obtained results have shown that the degree of protective power of the aquifer against acidification depends on a number of factors. An important factor is the composition of soil which is a product of natural weathering of the bedrock and the rate of buffering reactions. Neutral or weakly alkaline surface water at Pluhuv Bor shows that basic rocks can produce soil with a greater protective power against acidification, in spite of a low proportion of groundwater in the surface water.

The second important factor is the distance between the monitored catchment and the source of the pollution. Some acidic gases (SO_2, NO_2) are accumulated on coniferous trees by adsorption and then oxidised to strong acids. These adsorbed gases, as well as dry deposition, result in the heaviest acid loading at any locality.

The third factor is the duration of exposure of the soil to acid rain. The soil composition, including the soil buffer capacity, may change during the course of time. The first step is a decalcification followed by a hydrolysis of aluminosilicates. The mechanism of the hydrolytic reaction may change depending on the acidity of the infiltrating water.

The Krusné hory Mts. have been exposed to unfavourable conditions already since the 19th century. Mining for lignite and its combustion in power plants located in the Krusne hory piedmont basins began already in 1860 and culminated in 1988 (Fig. 4). Only in the last decade has there been a decline in mining for lignite and

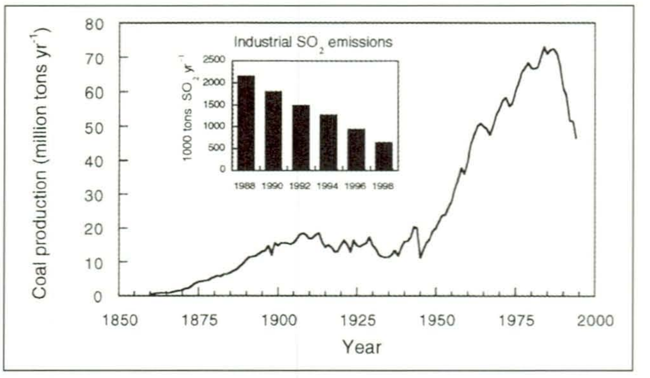

Fig. 4. Trends in annual coal production in the northern Czech Republic (Most basin). The small inset box shows the nationwide industrial emissions of SO_2 (from Novak et al. 2000).

consequently in a reduction of emissions. The prolonged impact of acid atmospheric deposition resulted in a decrease in the buffer capacity of soil of the Krusne hory crystalline complex. Consequently, the drained waters suffered from a decrease in the concentration of HCO_3^- ions and a very slow decrease in the contents of SO_4^{2-} ions (Fig. 5).

A conspicuous decrease in the buffer capacity of the soil layer of the Krusné hory Mts. has recently been supported by a study of the Jezerí catchment (Novák et al. 2000). Isotope analyses of sulphur in water entering and leaving the catchment show that the sulphur in the runoff comes from the soil horizon. Consequently, it represents a secondary source that was accumulated over long decades and from which the sulphur is gradually leached and washed out. The study by Novák demonstrates that approximately 30% of the total content of sulphur in drained water comes from organic matter confined to the upper humic soil horizon.

The negative role of the SO_4^{2-} storage in the weathered substrata has also been demonstrated in the German exper-

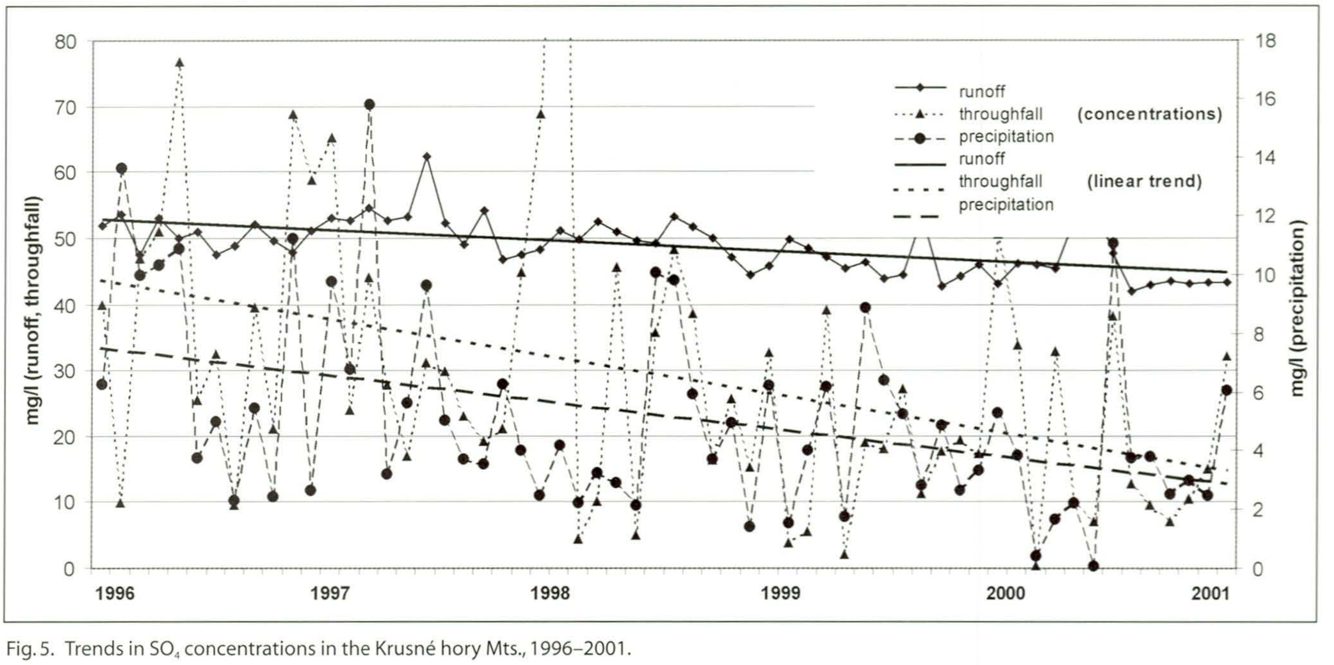

Fig. 5. Trends in SO_4 concentrations in the Krusné hory Mts., 1996–2001.

imental catchment Lehstenbach in northern Bavaria (Lischeid et al. 2000, Manderscheid et al. 2000).

Rock massifs such as the Krusné hory gneisses, which are more resistant against acidification, can for longer periods of time protect groundwaters against the impact of acid rains. On the other hand, after a reduction in the impact of acid deposition, it may take a long time to revert to the original conditions and the rock massif may, in contrast, maintain or support the acidification. Groundwater acidification in such aquifers will not be easily reversed by a decrease in SO_4^{2-} deposition because of the release of previously stored SO_4^{2-}. This appears to be the major reason for the recorded differences in groundwater quality between the Jezeri and Na Lizu catchments.

Regardless of the reasonable harmony between correlated runoff parameters and chemical composition of water, an unexpected discrepancy has been recorded in some periods. The period between February and June 1997 in the Jezeri catchment may serve as a typical example of such discord. A flood wave associated with snow melting and increased rainfall during March led to a decrease in the share of groundwater in the total runoff. This condition, however, is surprisingly not reflected in a lowering of pH in the surface water that remained more or less stable at about 5.4. This fact can be explained by the chemical composition of the rainfall because the pH of atmospheric water in the same period gradually increased by two orders of magnitude up to 6.0. This means that there was a period when the infiltration of rainfall had an unexpected alkaline reaction.

This example clearly demonstrates the complexity of the whole problem, which cannot be simply reduced to the relationship between the rock massif and water. Chemical analysis of a water sample from a stream always represents a mixture of surface and groundwater or even atmospheric water, and their mutual proportions may vary considerably. On the other hand, it is obvious that the volume of groundwater in runoff remains one of the most important factors influencing the finite quality of the drained water from the catchment. Therefore, the degree of groundwater acidification should not be neglected.

Acknowledgements

I would like to thank Drs. David Banks and John Mather for their helpful and constructive reviews, which significantly improved an earlier version of this paper; and also Mrs. D. Fottová for the valuable data from the GEOMON network.

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