Acidification of groundwater in the Bohemian Massif

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Hrkal, Z. 1992: Acidification of groundwater in the Bohemian massif. *Nor. geol. unders. Bull. 422, 97-102.*

An investigation of regional groundwater acidification in the Krusné Hory mountains of northern Bohemia has been carried out. It is based on a comparison of two groundwater chemistry data sets, from the years 1955-1969 and 1980-1990 respectively. The survey uncovered a fivefold increase in the average concentration of NO_3^- from 0.06 meq/l (4 mg/l) to 0.31 meq/l (19 mg/l) over the 25 year period, and a halving of the groundwater's average alkalinity. The most acidified groundwaters were found at the highest altitudes, but the most rapid rate of change in the groundwater's chemistry was found lower down, where, for example, NO_3^- concentrations have increased by a factor of 10 over the study period.

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Introduction

Bohemia (the western territory of the Czech republic) is one of the most polluted regions in the world. Extensive use of poor quality fossil fuels has led to a decline in the pH of precipitation and to a high rate of atmospheric deposition of, for example, nitrogen and sulphur species. The effects of such 'acid rain' have been studied in a number of countries, and have been particularly widely discussed and publicised in the Scandinavian lands. In spite of the fact that the soils' buffering capacity is generally somewhat higher in the Bohemian Massif than in much of Scandinavia, dramatic acidification of the Bohemian environment, particularly of surface waters, is observed. For example, the pH value in lakes near the German border in the south of Bohemia declined from 6.5 - 7.0 in 1936 to 4.5 - 4.8 in 1976 (Fott et al. 1980). One can also chart a decline in the alkalinity of Bohemia's main watercourse, the River Labe, at a rate of around 0.004 meq (0.26 mg) HCO_3^-/l/yr since 1898 (Paces 1982). In contrast, the extent of acidification of groundwater was largely unknown until recently, it being assumed that its vulnerability to acidification was very low. Studies of small catchments provided some warning that acidification of groundwater might be occurring (Jezersky 1991), but only short-term data from such sites was available. A study of regional changes in groundwater chemistry was therefore initiated by the Geological Survey of Prague. Preliminary results from the Krusné Hory mountains give serious indications of extensive groundwater acidification. It is hoped that the results from this study will be of use to hydrogeologists from lands where acidification of groundwater appears to be less advanced (e.g. Scandinavia). The results should assist in predicting the chemical changes that can be expected with increasing degree of acidification.

Description of the chemical data and the investigated area

The investigation is based on a comparison of two sets of groundwater chemistry data, from the years 1955-69 and 1980-90 respectively. The data refer to samples collected from springs from the Proterozoic metamorphic rocks (schists, migmatites) and Palaeozoic granites within a 1200 km² area of the Krusné Hory mountains in North Bohemia (Fig.1). To the south of the range lies the Northern Bohemian Rift Valley, active since Cretaceous times. The part of the valley between Sokolov and Teplice contains extensive deposits of freshwater Neogene sediments, including lignites, or brown coals, with high sulphur contents (8-12%) (Tyrácek et al. 1990). These ligni-

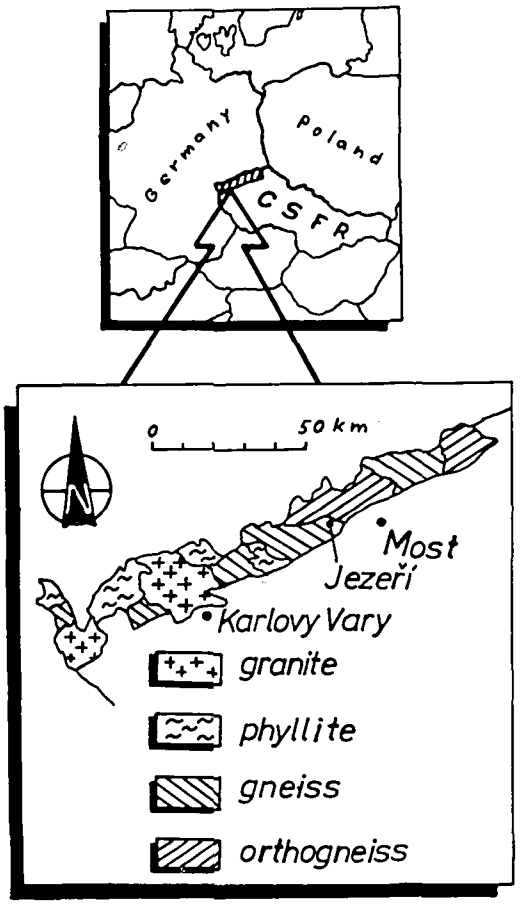

Fig.1. Schematic geological map of the studied area.

tes are widely burnt in power stations and factories along the Rift Valley, releasing considerable quantities of atmospheric pollutants, including oxides of sulphur and nitrogen. Each year the industrial complex in the valley emits some 2-2.5 x 10^6 tons of SO_2, and the power station at Sokolov alone emits 0.6-0.8 x 10^6 tons SO_2 per year (Le Baill 1986). To the north of the mountain range lies the border with the former D.D.R., where industry and power stations also emit large amounts of similar pollu-

Table 1. Concentration of principal ions in rainfall in the Krusné Hory mountains region (in meq/l) - medians for period 1976-82 (according to Moldan et al 1983).

Na^+	9.6×10^{-1}	NO_3^-	5.64×10^{-2}
K^+	5.6×10^{-1}	Cl^-	1.49×10^{-2}
Mg^{++}	1.07×10^{-2}	$SO_4^=$	8.6×10^{-2}
Ca^{++}	5.04×10^{-2}		
NH_4^+	7.71×10^{-2}	pH	4.19

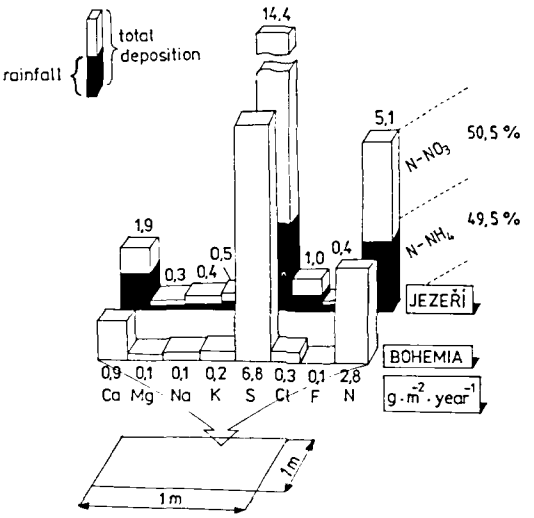

Fig.2. Annual atmospheric deposition of various elements - average for Jezeří small catchment in the Krusné Hory mountains, compared with average for Bohemia (according to Moldan et al 1987)

tants. Thus, for the Krusné Hory mountains, there is no preferable wind direction! The average altitude of the Krusné Hory region is approximately 750 m above sea-level, with a maximum altitude of 1244 m. The average annual precipitation is between 900 and 1100 mm, and contains high concentrations of $SO_4^=$ and NO_3^- (see Table 1). The study area is devoid of agricultural activity, and up to the early 1970s was covered by dense forest. In the late 1970s, within a relatively short space of time, practically all the conifers above an altitude of 800-900 m suffered defoliation and died back. One of the reasons for this may lie in the high level of 'acid' atmospheric deposition (Fig. 2), with an extremely high fallout of sulphur and nitrogen species (Moldan et al. 1987).

The study consisted of the statistical analysis of 166 chemical analyses from the period 1955-69, followed by resampling of 103 locations in the decade 1980-90. Where possible, the sites were resampled in the same season as the original sampling. For each spring, values of pH and concentrations of Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, NH_4^+, Fe, Al, Cl^-, NO_3^-, $SO_4^=$ F^-, and HCO_3^- were determined. Unfortunately, Al determinations were not consistently available for the old data set, and the poor quality of old pH value did not allow a comparison (Table 2).

Groundwater quality changes in the Krusné Hory mountains

Comparison of the average concentrations of principle cations and anions in the periods 1955-69 and 1980-90 reveals dramatic changes (Fig. 3). Most effort was dedicated to documenting changes in the average values of HCO_3^-, NO_3^-, $SO_4^=$, Ca^{2+}, which seem to be among the most reliable indicators of acidification (Grimvall et al. 1986). The most significant changes were found in the concentrations of HCO_3^- and NO_3^-. The average NO_3^- concentration of 0.31 meq/l (19 mg/l) is not exceptionally high in the context of the EEC limit for drinking water of 50 mg/l (0.81 meq/l), nor in the context of the fact that many aquifers in the central part of the Bohemian Massif are characterised by a level of 200 mg/l (3.2 meq/l) or more of NO_3^-. These latter values of NO_3^- are, however, largely connected with agricultural activity, such that a value of 0.31 meq/l (19 mg/l) in an area devoid of agriculture must be regarded as very significant. In fact, the study reveals a fivefold increase in NO_3^- concentration in the Krusné Hory region over the 25 year period of study. Such an increase must be caused directly by atmospheric deposition, or, according to some international experiences, by rapid changes in vegetation cover. Deforestation generally results in major changes in groundwater quality (Borman & Likens 1970, Henriksen et al. 1989). Vegetation can absorb and metabolise a certain

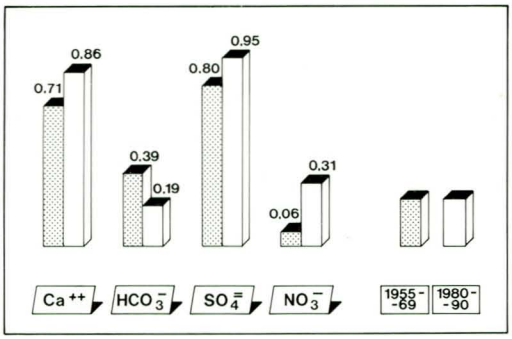

Fig.3. Changes in concentration of Ca^{2+}, HCO_3^-, $SO_4^=$ and NO_3^- in groundwater from springs in the Krusné Hory mountains between the periods 1955-69 and 1980-90 (all concentrations in meq/l).

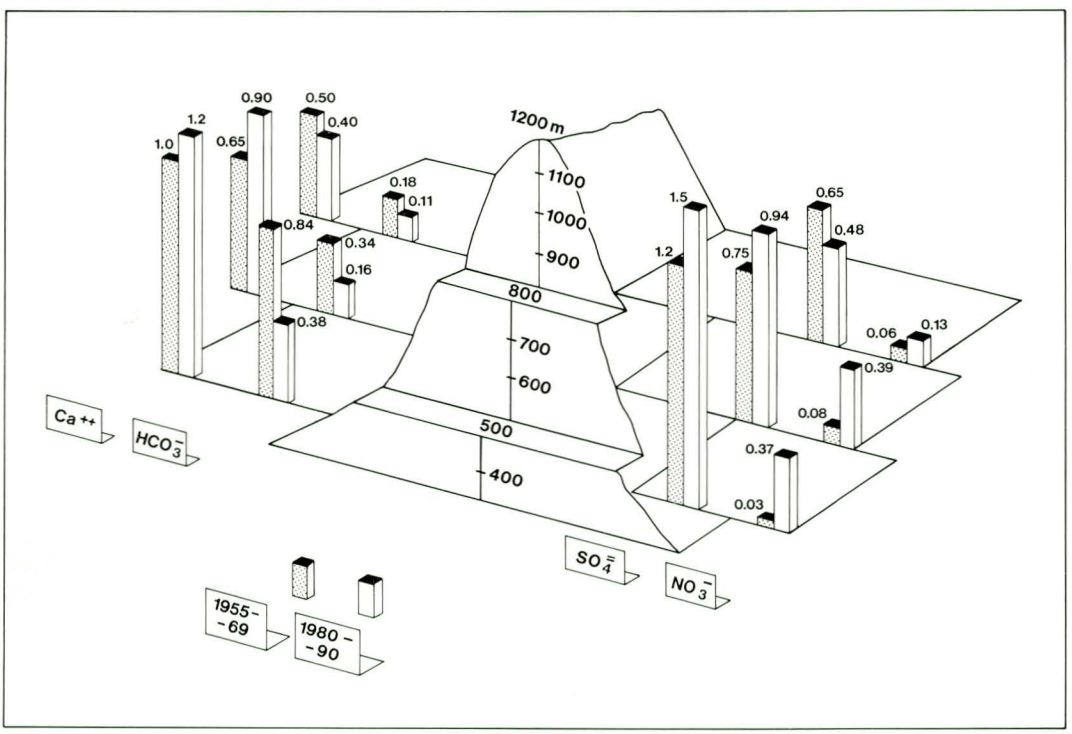

Fig.4. Changes in concentration of Ca^{2+}, HCO_3^-, $SO_4^=$ and NO_3^- in groundwater from springs at various altitudes in the Krusné Hory mountains between the periods 1955-69 and 1980-90 (all concentrations in meq/l).

Table 2. Summary of chemical data from sampled springs (in meq/l; TDS in mg/l)

	1955-69				1980-90			
	N	max.	min.	ave.	N	max.	min.	ave.
Na^+	166	6.74	0.03	0.32	100	2.00	0.05	0.27
K^+	166	0.66	$3x10^{-2}$	0.08	100	0.74	$3x10^{-1}$	0.09
Li^+	40	0.04	$1x10^{-1}$	$6x10^{-3}$	100	0.01	$1x10^{-1}$	$1x10^{-3}$
NH_4^+	37	0.05	$5x10^{-2}$	$7x10^{-3}$	100	0.08	$5x10^{-2}$	$3x10^{-3}$
Mg^{++}	166	2.25	$8x10^{-2}$	0.36	103	1.76	0.08	0.44
Ca^{++}	166	5.44	0.03	0.71	103	3.13	0.13	0.86
Mn^{II}	41	0.14	$2x10^{-2}$	$5x10^{-3}$	103	0.02	$2x10^{-2}$	$1x10^{-3}$
Fe^{II}	139	0.65	$4x10^{-2}$	0.03	88	0.45	$4x10^{-2}$	0.02
Al^{III}	—	—	—	—	30	0.11	$1x10^{-1}$	0.02
Total				1.518				1.705
Cl^-	166	1.07	0.07	0.25	103	2.53	0.04	0.25
NO_3^-	71	0.65	$2x10^{-2}$	0.06	103	2.14	$5x10^{-1}$	0.31
HCO_3^-	166	6.19	$2x10^{-2}$	0.39	103	0.85	$2x10^{-1}$	0.19
$SO_4^=$	166	2.84	0.14	0.80	103	2.73	0.21	0.95
F^-	42	0.11	$5x10^{-2}$	$9x10^{-3}$	58	0.03	$5x10^{-2}$	$7x10^{-3}$
Total				1.509				1.707
TDS	166	760	31	107	103	478	15	121

amount of atmospherically deposited nitrogen. Deforestation removes that capability, and the amount of nitrate leached down into groundwater typically rises dramatically.

An altitude analysis yielded unexpected results (Fig.4). Previous studies (Kinkor 1987, 1988) had led to the belief that acidification of groundwater would only exist at the highest altitudes, above 700-800 m. It is above this elevation that one can find dying forest, extremely high atmospheric deposition, rapid run-off and short groundwater residence times. A previous 'small catchment' study indicated a tendency towards lower pH values in springs situated above 800m compared with lower-altitude springs (Jezersky 1991). The average pH of high altitude springs was 5.4, compared with a value of 6.5 for springs in the foothills. Figures 4 & 5, however, show that the largest *changes* in acidification-related species during the 25-year period of study occured at lower elevations. Total dissolved solids (TDS) at lower altitudes increased from 166 mg/l to 194 mg/l (Fig.5), NO_3^- increased ten times, and the average HCO_3^- concentration declined from 0.84 meq/l (51 mg/l) to 0.38 meq/l (23 mg/l) (Fig.4).

Altitude-related information does *not* confirm the presumed role of deforestation in the increase in groundwater nitrate concentrations. On the contrary, the largest changes in nitrate concentrations were recorded at an elevation of around 400 m, where the hillside still boasts relatively good forest cover.

There are several hypotheses which may help to explain this pattern. The total atmospheric deposition, being the main source of $SO_4^=$ and NO_3^-, consists of two parts - wet and dry deposition (Fig.6). The dry deposition consists of small dust particles and gases which fall

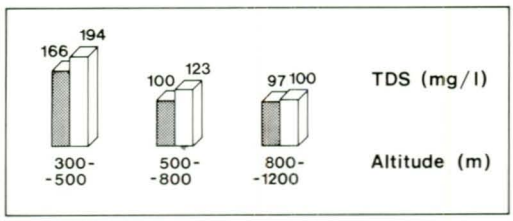

Fig.5. Changes in total dissolved solids in groundwater from springs at various altitudes in the Krusné Hory mountains between the periods 1955-69 (black column) and 1980-90 (white column).

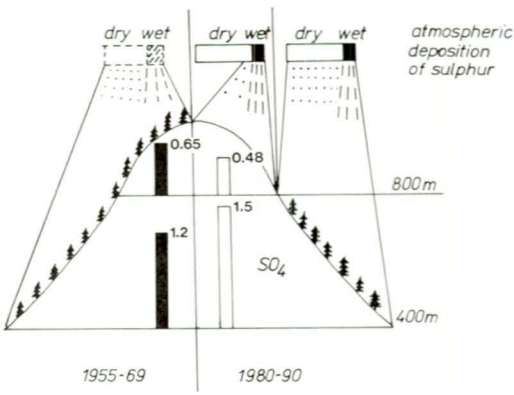

Fig.6 Hypothetical explanation of changes in concentration of $SO_4^=$ in groundwater at various altitude between the periods 1955- 69 and 1980-90 (concentrations in meq/l).

out onto the leaves of vegetation/forest, and which, during rainy episodes, are washed down to the soil and ultimately to groundwater. The removal of forest cover could conceivably reduce the proportion of dry deposition, due to the associated reduction in available surface area which could capture/absorb dust particles and gas.

In addition, vegetation/forest-cover leads to increased evaporation from leaves, and increased evapotranspiration from the soil zone. Removal of forest would therefore result in less evapotranspiration and a more dilute recharge-water reaching the water table.

A combination of these phenomena might explain the reduction in sulphate concentrations in groundwater at high altitudes during the study period, and (assuming that the lower slopes have always been more densely forested than the higher) the highest concentrations of sulphate, even in 1955-69, being found at lower altitudes (Fig. 4). As far as nitrate is concerned, two antagonistic trends may be occurring at the same time. The disappearance of forest cover might:

(a) result in increased NO_3^- in groundwater, as the vegetation layer's capacity to absorb and metabolise atmospherically deposited nitrogen has been reduced;

(b) reduce the fallout of dry atmospheric deposition (which, for sulphur and nitrogen, is decisive in the Krusné Hory (Fig.2)), and reduce the vegetation layer's evapotranspirative concentration effect on recharge water. Both of these would result in decreased NO_3^- concentrations in groundwater;

NO_3^- concentrations at altitudes above 800m have increased over the study period, but possibly because of the dominance of the factors under (b) above, at lesser rate than at lower altitudes. A rather paradoxical conclusion follows - that deforestration as a result of 'acid rain' can slow down further deterioration of groundwater quality.

The results of the study indicate that groundwater acidification is furthest advanced at the higher altitudes of the Krusné Hory mountains, where the carbonate buffer capacity is exhausted and the HCO_3^- concentrations are so low that they permit a decline in pH (Jezersky 1991). On the lower slopes, HCO_3^- concentrations are higher, and the pH exhibits no change at present. However, the decline in alkalinity at these altitudes is so rapid that pH decreases can be expected soon.

Discussion

It is evident that, in the region of the Krusné Hory mountains, important changes in groundwater quality have occurred during the last 25 years or more, of a character similar to trends tentatively observed in Norway and Sweden in connection with 'acidification' of the environment. The changes appear, however, to be more advanced than those documented from Scandinavia. At present, research in Bohemia is being carried out on two scales, each of which poses its own particular problems:

(a) 'Small catchment' studies supply very accurate, and specific, chemical data, but available results cover a very limited time-span, and represent local conditions. The results are thus difficult to generalize.

(b) The Krusné Hory study detailed in this article is an attempt at a more regional view. The investigation is based on a dense network of relatively old data. The data, however, are not quite old enough! Due to the long history of industrial activity in the region, the original, pre-industrialization background data are largely unknown.

Acknowledgement

I am grateful to Mr. David Banks at the Geological Survey of Norway, who has contributed with many useful comments on the manuscript.

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Manuscript received July 1991; revised typescript accepted November 1991.