Groundwater Quality Development in Area Suffering from Long Term Impact of Acid Atmospheric Deposition – The Role of Forest Cover in Czech Republic Case Study

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1. Introduction

About 84% of the Czech Republic is covered by so called hardrocks, igneous, metamorphic and strongly cemented rock. Such kind of rock environment is widespread throughout the world, the total extension is estimated at about 20% of present land surface, i.e. approximately 30 millions km² (Krásný 1999). From the hydrogeological point of view only near surface aquifer is important. Aquifer thickness is generally in the range of tens of meters and permeability decreases downwards. Nevertheless shallow hardrock aquifer is of major importance in generation of regional groundwater runoff and, consequently, groundwater resources development. Over the large areas hardrock aquifer is only source of drinking water. Problem is that shallow aquifer confined to crystalline rocks is very vulnerable to a decline in atmospheric precipitation and infiltration and exploitable yield should be very unstable.

Hardrock aquifers in Central Europe and in the Czech Republic in particular pose a specific problem consisting in gradual degradation of quality of ground waters caused by long-term acid atmospheric deposition. During the last few decades a dramatic change took place so that the proportion of major cations and anions resulted in change of chemical type of ground waters. Due to significant decrease in pH, the metals bound in the rock massif were mobilized and their enhanced contents in ground waters resulted in damage of mountain ecosystems. In extreme cases there occurred a failure in water supply, which could have been linked with worsening of groundwater quality.

Significant damage to national economy caused by acidification initiated a range of projects focused on the investigation of interaction between atmospheric deposition and biosphere and hydrosphere. The vast majority of these activities were based on the monitoring of the
small catchments of which areal extent did not exceed 1 km² and in which a mass balance was measured and established. The input of bulk deposition and throughfall in the system and then the output in form of chemical composition of groundwater leaving the catchment were measured. Detailed studies were focused on individual factors influencing the quality of water drained from the catchment. The investigation revealed that besides the character of rock environment, the vegetation cover, the forest in particular, plays an essential role in the quality of ground waters.

The rain washes down into soil dry deposition, dust particles and aerosols caught on leaves and needles of trees. These particles represent in the Czech Republic 2/3 of the total dry deposition (Havel et al. 1996). The intensity of this process is closely connected with the age and type of the forest (Malek & Astel 2007). Old conifers in general exhibit the highest ability to catch dry atmospheric deposition (Likens & Bormann 1995). The acidification is accelerated in particular by spruce conifers that mostly intensify the deposition of H⁺ ions (Probst et al. 1992). For instance, Bergkvist and Folkeson (1992) found throughfall in spruce forest in comparison with beech trees and birch to have exhibited three times greater deposition of SO₄ and even eight times greater deposition of H⁺. Also Jezeří catchment in the Krusne hory exhibited 49.3 kg S ha/yr under conifers and only 11.6 kg S under deciduous trees in 2000, while bulk deposition in an open area was only 8.1 kg S (Fottová 2003). These data support the argument against planting coniferous monocultures in areas with elevated air pollution. However, apart from this the quality of groundwater is also influenced by internal biological cycle of the forest (Parker 1990).

The atmospheric precipitation only after its passage through vegetation cover is infiltrated into the ground being first in contact with soil, unsaturated and finally with saturated zone of the rock massif. The groundwater gradually changes its chemical composition and the acidity of atmospheric deposition is attenuated by ongoing buffer reactions. During the first stage of acidification, which is more or less discreet, the pH remains stable because the acid deposition is buffered by HCO₃⁻ ions of which concentrations gradually decrease. Once the bicarbonates are consumed during this process the pH decreases and further progress in acidification is buffered by humic compounds and aluminum (Fottová 2003, Hruška & Krám 2003).

However, changes taking place in groundwater have also a backward effect on the health of the given forest. Low contents of calcium and magnesium and high concentrations of metals mobilized by low pH pose the first problem. Aluminum and beryllium appear to be the most dangerous elements for root system of trees as far as toxicity is concerned (Puhe & Ulrich 2001, Navrátil et al. 2002). According Ebben (1991) particularly spruce forest (Picea abies) is extremely sensible to high concentration of toxic metals.

However, the obtained results have only limited informative value for regional hydrogeological considerations as they provide although very exact data, but relating to very small area often not exceeding a few hectares. Moreover, the hydrochemical data from surface streams characterize an overall runoff from the catchment, which represents a mixture of surface and groundwater of which the mutual relationship varies considerably in the course of the year. Consequently, to separate data characterizing only the quality of groundwater from data related to the overall runoff was found very difficult (Hrkal et al. 2002).
So far acquired data became a motivation for the assessment of groundwater quality and its development on regional scale. Consequently, three mountain regions in Bohemia that were most affected by atmospheric deposition were selected for investigation—specifically the Krusne hory Mountains (Erzgebirge), Jizerské hory Mountains and Krkonoše (Giant) Mountains. All these regions suffered in recent past from large ecological damage resulting in extinction of the forest cover due to acid atmospheric deposition. The results of investigation of small catchments revealed close links between the type and/or health of the forest and the quality of groundwater in the catchment. Therefore, the project was focused on the assessment of the role, which the forest plays in the quality of groundwater on regional scale in an environment that is strongly affected by acid atmospheric deposition.

2. Description of pilot sites

Three mountain regions were selected as the pilot sites for investigation—Krusne hory Mts. (Erzgebirge), Jizerské hory Mts. and Krkonoše (Giant) Mts. (Fig.1).

![Fig. 1. Situation of pilot areas](image)

All these areas suffered in recent past from large ecological disaster resulting in extinction of the forest cover evidently due to acid atmospheric deposition. All three regions are similar to one another as far as their geology and topography are concerned, but differ significantly from each other by the length and intensity of acid atmospheric deposition. Krusne hory Mts. were exposed to negative impact of acid atmospheric deposition for more than one century of which intensity culminated on the turn of 1970s and 1980s. The peak of negative impacts of acid precipitation occurred ten years later in the Jizerské hory Mts and Krkonoše Mts. Another difference between these regions is the level of environmental protection. While in the Krusne hory Mts only small areas are protected, the Jizerské hory Mts as a whole are Protected Landscape Area and Krkonoše Mts belong among most protected areas having a status of National Park.

2.1 The Krusne hory Mts.

The Krusne hory Mts. were selected as a model region because they suffered from uncontrolled anthropogenic activities. The total area of the investigated part of Krusne hory
Mts. is 1392 km\(^2\). The region is a part of the so-called "Black triangle" close to a junction of borders between Czech Republic, Germany and Poland. The region is characteristic of strong accumulation of heavy industry, chemical plants, power stations and open cast mines for lignite, which were in operation for more than forty years. Huge open cast mines, some of them as much as 300 m deep completely changed the landscape of the piedmont area resembling a "moonscape" exhibiting entirely different hydrological regime. Burning of low-grade lignite high in sulfur (ranging between 8 and 12\% - Tyracek et al. 1990) in local power stations resulted in extremely high values of acid atmospheric deposition, which caused acidification of all elements of the environment. As a consequence, the apical parts of the mountain range suffered from mass extinction of the forest cover, which led to stronger erosion, degradation of surface and groundwater quality including negative impacts on hydrological regime in general.

The situation has improved considerably during the nineties due to several factors and imposed measures, which were functioning in the area on parallel lines.

Krusne hory Mts. build a natural boundary between the Czech Republic and Germany. The mountain range is elongate in NE-SW direction with highest peak Klínovec 1224 a.s.l. The area under consideration belongs to slightly cool-to-cool climate with higher total precipitation mostly in areas more than 800 m a.s.l. where long-run rainfall is close to 1000 mm. Due to relatively low average atmospheric temperature (between 5°C and 7°C) the precipitation in form of snow lasts for considerable part of the year.

The potential natural vegetation in the Krusne hory Mts. is characterised by mixed forest of European beech, Silver fir, Norway spruce with a smaller admixture of birch oak and maple (Jankovská 1992). During the last centuries, forests in the Krusne hory have been dominated by Norway spruce. In the 1950s, before air pollution substantially increased, Krusne hory Mts. were predominantly covered by spruce monocultures with a small admixture of beech and larch. The first damage to the forest stands appeared in 1947, when the first symptoms to soil acidification due to enhanced air pollution has been observed (Nemec 1952). Since the 1950s to early 1970s, the area of damaged forest has slowly but continuously spread. Marked acceleration of forest health deterioration was observed after 1979 and was triggered by a temperature drop in 1978. Following figure shows the development of damage to spruce stands over the period 1960-1990.

In 1960 more than 50\% of stands were classified as healthy. Later on the healthy stands disappeared and the share of clearcuts increased. The “harvested stands” category is sum of all spruce stands cut due to the forest decline. In 1990 more than 50\% of the spruce stand was cut. Extending cutting have occurred, namely in higher elevation of the mountains, e.g. above 700 m a.s.l. where almost all older stands were harvested.

In many places, a site preparation prior to reforestation was done. One of the most common methods was topsoil removal with bulldozers, which was applied on almost 4000 ha. This method was introduced to increase the productivity of reforestation. It was expected to level the soil surface for planting machines and even to improve the soil’s physical and chemical properties. However, research results show the rather negative influence of this method on soil fertility and growth of newly planted seedlings.
The combination of different stress factors limited the use of local tree species i.e. spruce and beech, for reforestation. Forest regeneration was oriented to the establishment of new (so-called “substitute” or “emergency”) forest stand composed of free species more tolerant to air pollution.

The dominant species in the “substitute” stands are birch, Blue spruce and Mountain ash. The main goal of establishing such “substitute” stands is to recovery of ecological function of forests in the affected regions, as species used have the most important pioneer function. The large scale usage of these tree species substantially changed the tree species composition of the new forest (Fig. 3.).
2.2 The Jizerské hory Mts.

The Jizerské hory Mts. constitute the northern morphological boundary between the Czech Republic and Poland (see Fig. 1). The altitude of the relatively flat crest of the mountain range slightly exceeds 1000 m above sea level. The Jizerské hory Mts. belong among the wet regions with annual total mean rainfall corresponding to 800 – 1700 mm. Due to the topography of these mountains there exists a thick drainage pattern. The only natural water surface areas are peat bogs of which thickness varies within a few meters. More than 50 peat bogs of which the total areal extent exceeds 250 hectares exist in the mountains.

Geologically the study area is divided into two domains: the majority area is underlain by various types of granite of the Krkonose-Jizerske Mts. massif. Due to its siliceous character, the area of the granite massif contributes to acid character of local groundwaters. Only the northernmost part of the study area, composed of Proterozoic chlorite-sericite phyllite, amphibolite and mica schist, yields small amounts of acid of the groundwater.

The character and type of rock mantle and Quaternary alluvium generally play very significant role in other regions, but in the Krkonose-Jizerske granite is weathering into sandy eluvium showing equal character over the entire area. Only its thickness varies to certain degree. Some more or less random data revealed that greater thickness, as much as about 15 m, are expected to occur in depressions and on slopes, thus in areas of lower altitude.

Forest is the main natural vegetation cover in mountains occupying 274 km$^2$ of the total area of 368 km$^2$. Woodless areas are scarce being mostly confined to apical debris covered parts, peat bogs and wetlands. The original forest cover consisted mostly of beech, spruce and fir. The original forest cover remained untouched until the German colonization in the 13th century during which the forested area was reduced. The apical parts of the mountain range maintained their original features until the 16th century and the logging began as late as in the 17th century. Glassworks consumed the majority of wood that was used as a fuel. The plunder of forests started in the 18th century when deciduous and mixed forests became completely extinct at numerous sites. Artificial spruce monoculture planted from the 19th century turned out to be not very suitable because since the very beginning of the 20th century these spruce forests suffered from catastrophic blow-downs and calamities. In the middle of 1960s the spruce (Picea abies) formed 85% of the forest while the share of beech (Fagus sylvatica) was only 9%. Poor health of the spruce forest was gradually worsening and finally completely damaged by acid atmospheric deposition from power plants in Poland (power plant Turów) and in the former German Democratic Republic (power plant Hirschfelde). Mass extinction of the forest, due to immunodepression of forest species took place on flat apical parts of the mountain range and the dead forest was completely lumbered in the 1970s and 1980s. This area was then gradually forested by planting of a very limited number of tree species. Blue spruce (Picea pungens) was introduced in addition to autochtonous Norway spruce.

2.3 The Krkonoše Mts.

The Krkonoše mountain crest is 35 km long constituting a natural boundary with Poland. The apical parts of the mountain range with elevations around 1400 m above sea level are flat but its north-eastern slopes are plunging steeply into Poland. The opposite side of the
mountain range is dissected by deep valleys but in general it plunges much more gently southward. Krkonoše Mts. are the highest mountain massif of the Czech Republic with the highest peak Sněžka 1603 m a.s.l.

As concerns the climate the Krkonoše Mts. are the harshest mountain ranges of which the apical parts can be correlated with the climate of Greenland shores. The mean maximum of snow cover attains as much as 2 meters and the average annual temperature fluctuates between 0 and 2°C.

Geological structure consists mostly of metamorphic rocks, mainly phyllites and gneisses accompanied by a granite massif and rare effusive rocks. Rare crystalline limestones occur in the eastern part of the mountain range. Two phenomena participated in creation of the present form (topography, morphology) of the mountain range. Tertiary alpine folding during which a gradual uplift and arching of the mountain range took place and resulted in today’s altitude and shape. River erosion and activity of continental glacier in particular are responsible for the current and definite shape of the mountain range.

Krkonoše Mts. forms a natural water-divide between the North and Baltic seas and where numerous rivers rise including the river Labe (Elbe).

The present forest cover underwent a dramatic development and change since the last ice age. Characteristic vegetation cover after the recession of continental glacier consisted of pine, oak, hazel, lime and elm. Spruce, alder and dwarf pine began to grow there approx. 4500 years ago and two thousand years later beech began to appear in the mountains. The last principal changes in species composition took place roughly before 800 B.C when fir and dwarf form of Norway spruce and dwarf pine in apical parts of the mountain range began to grow. This kind of forest is considered to be the natural vegetation cover that continued until the 13th and 14th centuries when Krkonoše Mts began to be colonized. During the 16th and 17th centuries much of the forest was cut down mostly in connection with ore mining and production of charcoal when beech, ash and elm trees gradually disappeared. The reforestation began as late as in the 18th century when spruce monoculture...
imported from Austria was planted so that at the end of 19th century. At the first half of twenty century forest in the Krkonoše are dominated by Norway spruce (*Picea abies*), which occupies 87.7% of the forested area. The second most commonly present species is *Pinus mugo* (6.1%) which forms the three border in the higher elevations of the mountains. The share of other species (e.g. beech *Fagus sylvatica*, maple *Acer sp.* and birch *Betula sp.* was very low (2.8%, 0.5% and 0.8% respectively (Moravčík, Černý in Černý, Pačes 1995). Forestation of dwarf pine in tundra parts also took place.

However, the construction of power plants burning coal in the so-called black triangle had fatal consequences on the forest cover in Krkonoše Mts. where gradual extinction of forests in apical parts took place. The first observation of forest damage was made in 1979 (Tesař et al. 1982). Consequently, the forest covering almost 8,000 hectares was completely destroyed during the twenty years due to acid rains. Geographical distribution of spruce defoliation is uneven over the area of the Krkonoše Mts. The defoliation is found at sites in the western part of the mountains in higher elevation exposed to wind (Černý, Pačes 1995).

A managed and gradual forest regeneration consisting of planting fir and beech and to lesser extend even sycamore maple and rowan began in 1990s. Restoration of self-functioning ecosystems specific for the area of National Park is another remedy implemented in the Krkonoše Mts. The dead wood mass is intentionally left in the forest and its decay ensures the return of alkaline substances into soil thus reducing naturally its acidity and also supports species diversity. This step, however, has also some drawbacks because the current forest is not healthy enough and strong to be able to combat the bark beetle calamity since the dead wood left in the forest is a very risk factor.

### 3. Data available and methodology of the treatment

Three types of data acquired during prolonged periods of time were necessary to meet the designed project objectives. They include data on the development of dry and wet deposition, results of monitoring of chemical composition of ground waters and data on species proportion over the whole area and its development and on the forest health.

The development of ground waters chemistry on regional scale was reconstructed during the first stage of investigation and the results of groundwater quality were compared with the development of atmospheric deposition.

The second stage of studies was focused on the relationship between the quality of ground waters and the state of health of the forest in relevant catchments. The study was based on a network of catchments forming the infiltration areas of the monitored springs and defined within a Digital Elevation Model (grid 50 x 50 m) using ARCVIEW 3D Analyst software. All springs drained a shallow sub-surface aquifer confined to rock mantle and open fissures in metamorphic and magmatic rocks reaching a maximum depth of 30 m. Therefore, the hydrogeological divide was identical with the hydrological divide defined by local topography. A database of factors influencing the groundwater quality and governing changes in it was created for each catchment. The database included altitude above sea level of each spring, the areal extent of the catchment and the basic characteristics of the vegetation cover.

The following chapters provide a detailed overview of all data which were used for processing and considerations including description of methods of their acquisition.
3.1 Atmospheric deposition

Data on atmospheric deposition are available for three “pilot sites” that were monitored within the GEOMON project that has been operated by the Czech Geological Survey and is currently supported by the Ministry of Environment of the Czech Republic through the project SP/1a6/151/07. The above project is monitoring a network of catchments of which the Jezeří catchment in Krušné hory Mts. (JEZ), the Uhlířská catchment (UHL) in the Jizerské hory Mts and Modrý potok catchment (MOD) in the Krkonoše Mts were studied in detail. The basic programme of regular monitoring in individual catchments is the following:

- sampling of bulk precipitation - monthly cummulative samples
- sampling of throughfall precipitation - a mix of samples from the regular network of nine sampling stations in each catchment (for estimating the variability in vegetational density) - monthly cumulative samples
- sampling of the runoff from the catchment - basis
- acquiring data on the monthly precipitation amount in the unforested segment of the catchment
- acquiring data on the monthly throughfall
- a continual record of water level in the concluding profile of the catchment and determination a daily average outflow (from the consumption curve)

The sampling and analytical methods are uniform in the network which markedly raises the reliability of data and its mutual comparability (Fottová 1995, Fottová 2003). Accredited laboratories of the Czech Geological Survey run the following tests on all samples:

Na, Ca, K, Mg, S (SO₄), N (NO₃, NH₄), Cl, F, Mn, Fe, Zn, Al, As, Cd, Pb, Ni, pH, conductivity, DOC, DN.

Calculations of the element fluxes - input to the catchment of a defined area by bulk and throughfall precipitation and output from the catchment by surface runoff - is carried out from the data obtained in one hydrological year (from Nov. 1st to Oct. 31st of the following year). This is a question of monthly data on the concentrations of the monitored substances in both types of precipitation and runoff, monthly precipitation amount and the average daily outflow. The deposition of a particular element is counted as a sum of the 12 monthly deposition in units of mg/m³, calculated by multiplying the concentration in mg/l by the total monthly precipitation (both for bulk and throughfall data) in mm. The results for every element are presented in units of kg/ha/year.

The assessment of atmospheric deposition has especially been focused on trends of acidifying components so that the bulk and throughfall values of sulfur deposition as sulfates and nitrogen as nitrates are presented in graphic form (Figs. 5 and 6). An increase in pH that was higher in throughfall deposition was recorded evidently due to a desulfurization program.

As concerns sulfur (Fig. 5) a significant decrease in bulk as well as throughfall deposition (also including dry deposition) was recorded evidently due to a desulfurization program.
implemented by the government in 1994 – 1998. The graphs show a marked peak in 1996 in the Jezeří JEZ catchment where a curious situation occurred when, due to the installation of ash-fly separators, the concentration of solid particles decreased, but desulfurization units were not yet installed. As a consequence, the acid constituents were not neutralized by basic components contained in ash-fly which resulted in extremely acid atmospheric precipitation and even glaze ice. This in fact also affected the throughfall precipitation (Krejčí 2001).

![Graph showing sulfate atmospheric deposition on study areas between 1978 - 2009](image)

Fig. 5. Sulfate atmospheric deposition on study areas between 1978 - 2009

The deposition of nitrogen in the form of nitrates (Fig. 6) in both the Jezeří JEZ and Modrý potok MOD catchments showed no trend at all during the period 1994 – 2009, while in the Uhlířská UHL catchment some decrease in nitrogen content was recorded which is actually an exception within the whole of the GEOMON network of catchments. The deposition of nitrate nitrogen in the central part of the Czech Republic stagnated and in numerous catchments even decreased which a varying source of this form of nitrogen may be responsible for. This element came from emissions of power plants which were desulfurized but were still emitting nitrogen. Gasification of heating and recently a large increase in motor traffic are the new sources of nitrogen. The effect of aerosols, due to longer dry periods linked with changes in frequency of atmospheric precipitation, appears to be another source of nitrogen. It can be said that nitrogen after the year 2000 has become nationwide a more significant acidification element than sulfur.

The excess of nitrogen is manifested, for instance, by unnaturally high growth of trees. It is one of the primary reasons resulting in damage to the trees in combination with the direct effect of harmful substances on assimilation parts of the trees (including the effect of ozone) and acidification linked with mobilization of toxic metals in the soil. The weakened trees then have difficulties with secondary stressors such as sudden climatic changes, long dry periods in particular, insect pests or harmful fungi - Ascocalyx abientina (Hruška, Ciencala 2002).
Fig. 6. Nitrates atmospheric deposition on study areas between 1978 - 2009

3.2 Forest health and surface changes

Maps of defoliation and mortality of conifers derived from Landsat-TM/ETM imagery were compiled by the Institute for Economic Development of Forests within the grid 30 * 30 meters. Ten categories (graded in 10% divisions) expressing the degree of damage to conifers and also defining the average defoliation of conifers in the vegetation cover were used to assist interpretation of the analytical results. Category 1 indicates completely healthy forest, and category 10 indicates dead forest.

The oldest data come from 1984 and from continuous series of interpreted satellite images so that a time interval could have been selected which corresponded to a period when samples of groundwater were collected and analyzed.

Series of images enabled a detailed analysis of changes in the areal extent of forest in individual catchments, and could also be used to assess their health. An example of interpretation of the forest health and its development is shown in Fig. 7.

3.3 Quality of ground water

The quality of groundwater is a very dynamic phenomenon so that a very representative data set is needed for unbiased assessment of its areal and temporal variability.

Water samples were analyzed using standard methods in accredited laboratories of the Vodní Zdroje GLS Company and Water Research Institute. The flame atomic absorption spectrometry or optical emission spectrometry with induced plasma were used for the
determination of major and minor cations (Na, Mg, Ca, K, Mn, Li, Fe, Al, Zn, SiO₂), whereas trace elements (Cu, Pb, As, Cd, Be, Al, Co, Cr, Mo, Ni and V) were established by means of atomic absorption spectrometry with electrothermic atomization. Liquid ion chromatography was applied to determine SO₄, NO₃ and Cl. A glass electrode combined with pH meter (model Radiometer Copenhagen) was used for measurements of pH.

Fig. 7. Example of heath changes of forest cover in catchment No 17 in Krusne hory Mts. The earliest data on groundwater quality were gathered during the years 1959 – 1965 in the Krusne hory Mts. A database of analyses of single samples from 130 springs was compiled by the Czech Geological Survey during hydrogeological mapping undertaken at that time. The historical analyses gave only contents of the main cations and anions. A total of 62 springs from this group were reanalyzed for the same elements during the years 1965 – 1974 and 1979-1989 (during the same period of the year). Twenty six of these springs were again sampled and analyzed in 2000 – 2002 as part of the LOWRGREP 5. FWP EU project (Hrkal et al. 2003). This time, analyses were made at monthly intervals and trace elements and toxic metals were included.
The assessment of the Jizerské hory region is based on data collected in 37 small experimental catchments in which the variation in chemical composition of groundwater was monitored since 1971 until the present. The data come from springs which were analyzed in the frame of geological survey undertaken in the years 1971-1975 and 1983 – 1987 and then checked by single sampling in 1997, 2008 and 2009. The sampled springs more or less regularly cover the whole area of the Jizerské hory Mts. and can be considered a representative data set characterizing all phenomena, which may influence the resulting chemistry of local ground waters.

With respect to rather monotonous geology and lithology of the area studied that is built of granite, the resulting quality of groundwater is controlled by the chemistry of atmospheric precipitation and/or deposition, the time of interaction between the rock and water and the land-use. The first two phenomena are in the data set reflected by topography – altitudes above sea level of monitored springs vary between 340 m up to 1040 m. As concerns the
land-use, the forestry is the dominating type of exploitation, while meadows without any cultivation occupy only small part of the area. This is also reflected in the character of experimental catchments, which are forested and in many of them the forest covered as much as 100% of their total area.

Interpretation of the development of groundwater chemistry in Krkonoše area is based on a set of 34 springs. The data come from the years 1972 – 1974, and additional sampling took place in 1984 and 1994, and finally the very last sampling was carried out in 2008 and 2009. Experimental sub-catchments form two morphologically distinct groups which differ from one another by the type of vegetation cover and by climatic conditions.

The first group includes springs in apical parts of the mountain range with altitudes exceeding 1000 m above sea level of which catchment is mostly bare or only locally covered with dwarf pine, while the second group is located on mountain slopes with forest cover that underwent the above-mentioned development and changes.

4. Results and discussion

4.1 Comparison of the development of groundwater chemistry in pilot areas

The chemistry of ground waters in the Krusne hory area clearly shows the strongest affection by acidification among the three investigated regions. Weakly mineralized ground waters of $\text{Ca} - \text{SO}_4$, $\text{HCO}_3$ type were found to have been prevailing during the whole period of their monitoring. Unfortunately, no regional data on ground water quality are available from the 1980s in the Krusne hory area. On the other hand, data from the 1970s clearly point to major differences in average pH values of ground waters in the Krusne hory, Jizerské hory and Krkonoše areas. The contents of sulfates in ground waters from Krusne hory were in 1990s more than fivefold relative to $\text{HCO}_3$ component. A marked decrease in sulfates content was documented only the most recent analyses, but sulfates still remain the dominant component in Krusne hory Mts. ground waters.
The secondary concentration of sulfur in the soil horizon during the recent decades of atmospheric precipitation is believed to be responsible for this situation. At present, this accumulation is being progressively washed out again (Novak et al. 2000, Lischeid 2001). The study (Fottova et al. 2008) has shown that approximately 30% of the total sulfur content in the drained water comes from organic matter in the upper humic layer of the soil horizon. Consequently, the return of groundwater quality to the so-called “natural state” may take quite a long time.

<table>
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</table>

Table 1. Development of ground waters chemistry monitored in the years 1971 – 2009 in the Krusne hory area (an average from 26 monitored springs)

The results of monitoring revealed that similarly to Krusne hory the slightly mineralized ground waters of Ca - SO₄, HCO₃ type also prevail in Jizerské hory area. The chemistry of ground waters was found to be more or less stable in long-run. Nevertheless, some trend can be observed in some components, particularly those which indicate acidification. Local springs drain relatively shallow sub-surface zone of hardrocks where the time of interaction between the water and lithology is short so that the resulting chemistry of ground water is significantly governed by the chemistry of rainfall water. With regard to the decrease in acid atmospheric deposition, due to ecological strategy adopted by the Czech administration, the decrease in sulfates concentration from 33 mg/l in the 1970s down to 21 mg/l today is therefore not surprising. Similar trend exhibit also nitrates of which content dropped from 14 mg/l in 1970s to 4 mg/l currently. These values are already close to natural background.

Ground waters in Krkonoše region underwent an interesting development during the last thirty years. The characteristic type of groundwater in the 1970s up to the 1990s was similar to that in the Krusne hory and Jizerské hory areas, thus corresponding to Ca - SO₄, HCO₃. However, the most recent latest analyses undertaken in 2010 – 2011 revealed such a marked decrease in sulfates content so that ground waters can be classified to belong to Ca - HCO₃, SO₄ type, and in some cases even to the distinct Ca - HCO₃ type. This is not a random phenomenon, but a result of long-run trend supported by gradual increase in HCO₃ and decrease in sulfates content (Fig. 11).
Water Quality Monitoring and Assessment

Table 2. Development of ground waters chemistry monitored in the years 1971 – 2009 in the Jizerské hory area (an average from 37 monitored springs)

<table>
<thead>
<tr>
<th>period</th>
<th>Na mg/l</th>
<th>K mg/l</th>
<th>NH₄ ng/l</th>
<th>Mg mg/l</th>
<th>Ca mg/l</th>
<th>Al mg/l</th>
<th>Be ng/l</th>
<th>Cl mg/l</th>
<th>NO₃ mg/l</th>
<th>HCO₃ mg/l</th>
<th>SO₄ mg/l</th>
<th>F mg/l</th>
<th>mineralization mg/l</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1971-1975</td>
<td>5,21</td>
<td>2,01</td>
<td>0,04</td>
<td>4,85</td>
<td>17,6</td>
<td>?</td>
<td>?</td>
<td>9,40</td>
<td>14,21</td>
<td>16,91</td>
<td>33,1</td>
<td>0,12</td>
<td>113,5</td>
<td>6,52</td>
</tr>
<tr>
<td>1983-1987</td>
<td>6,32</td>
<td>1,72</td>
<td>0,12</td>
<td>3,42</td>
<td>17,3</td>
<td>0,19</td>
<td>?</td>
<td>8,81</td>
<td>11,6</td>
<td>14,91</td>
<td>27,6</td>
<td>0,17</td>
<td>90,7</td>
<td>6,06</td>
</tr>
<tr>
<td>1997</td>
<td>5,64</td>
<td>1,57</td>
<td>0,05</td>
<td>2,44</td>
<td>13,8</td>
<td>0,21</td>
<td>0,053</td>
<td>4,21</td>
<td>5,12</td>
<td>15,72</td>
<td>27,2</td>
<td>0,19</td>
<td>87,3</td>
<td>6,15</td>
</tr>
<tr>
<td>2008-2009</td>
<td>4,48</td>
<td>1,37</td>
<td>0,04</td>
<td>2,14</td>
<td>8,9</td>
<td>0,27</td>
<td>0,082</td>
<td>3,71</td>
<td>4,40</td>
<td>18,43</td>
<td>20,7</td>
<td>0,20</td>
<td>61,9</td>
<td>6,07</td>
</tr>
<tr>
<td>1971-2009</td>
<td>5,31</td>
<td>1,51</td>
<td>0,06</td>
<td>2,9</td>
<td>13,6</td>
<td>0,24</td>
<td>0,067</td>
<td>6,01</td>
<td>8,30</td>
<td>24,01</td>
<td>26,2</td>
<td>0,18</td>
<td>97,1</td>
<td>6,13</td>
</tr>
</tbody>
</table>

Similar trend can be seen in the case of nitrates of which contents vary around 5 mg/l. The ground waters monitored in the Krkonoše area always showed on average higher pH values relative to ground waters in the afore mentioned regions and also markedly lower degree of acidification. This is demonstrated by the fact that in the course of the 20th century, the pH at any of the monitored catchments did not fall below 6.0, not even at sites located at elevations exceeding 1 000 m above sea level.

Table 3. Development of ground waters chemistry monitored in the years 1971 – 2009 in the Krkonoše area (an average from 29 monitored springs)

<table>
<thead>
<tr>
<th>period</th>
<th>Na ng/l</th>
<th>K mg/l</th>
<th>NH₄ mg/l</th>
<th>Mg mg/l</th>
<th>Ca mg/l</th>
<th>Al mg/l</th>
<th>Be ng/l</th>
<th>Cl mg/l</th>
<th>NO₃ mg/l</th>
<th>HCO₃ mg/l</th>
<th>SO₄ mg/l</th>
<th>F mg/l</th>
<th>mineralization mg/l</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1971-1975</td>
<td>3,1</td>
<td>0,6</td>
<td>0,05</td>
<td>1,4</td>
<td>7,1</td>
<td>?</td>
<td>?</td>
<td>4,78</td>
<td>2,9</td>
<td>9,50</td>
<td>15,8</td>
<td>?</td>
<td>45,7</td>
<td>?</td>
</tr>
<tr>
<td>1983-1987</td>
<td>3,7</td>
<td>2,4</td>
<td>0,29</td>
<td>3,1</td>
<td>18,1</td>
<td>0,23</td>
<td>?</td>
<td>3,85</td>
<td>11,4</td>
<td>23,1</td>
<td>37,9</td>
<td>0,04</td>
<td>106,3</td>
<td>6,94</td>
</tr>
<tr>
<td>1997</td>
<td>2,6</td>
<td>1,0</td>
<td>?</td>
<td>1,9</td>
<td>9,8</td>
<td>?</td>
<td>?</td>
<td>2,45</td>
<td>7,1</td>
<td>20,5</td>
<td>13,7</td>
<td>0,06</td>
<td>68,0</td>
<td>6,86</td>
</tr>
<tr>
<td>2008-2011</td>
<td>?</td>
<td>?</td>
<td>0,16</td>
<td>2,9</td>
<td>11,5</td>
<td>0,20</td>
<td>0,02</td>
<td>2,50</td>
<td>5,7</td>
<td>36,4</td>
<td>9,5</td>
<td>0,03</td>
<td>74,2</td>
<td>6,42</td>
</tr>
<tr>
<td>1971-2009</td>
<td>3,0</td>
<td>1,3</td>
<td>0,19</td>
<td>2,5</td>
<td>11,3</td>
<td>0,14</td>
<td>0,23</td>
<td>2,86</td>
<td>6,32</td>
<td>27,75</td>
<td>14,23</td>
<td>0,04</td>
<td>69,17</td>
<td>6,62</td>
</tr>
</tbody>
</table>

Regardless of positive trends in groundwater quality it is obvious that some acidification processes still continue on regional scale partly due to persistent nitrogen deposition and partly also due to release of sulfur accumulated in long-run in soil profile. Characteristic chemistry of ground waters in these anomalous areas with prolonged pH lower than 5.5 is demonstrated in the following Tables 4 and 5.

These data clearly demonstrate fundamental differences in historical development of acidification of ground waters in all three compared regions. While in the 1970s almost 80% of springs in the Krusne hory area showed pH lower that 5.5, in Jizerské hory only 30% and in Krkonoše Mts all analyses revealed pH higher than 6.0. Very slow improvement can be demonstrated by analytical data obtained in the years 2008-2009 according to which 57% of local catchments still belong to the category of acidified ground waters. The number of acidified catchments in Jizerské hory area dropped to 19%.

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The common feature of analyses of ground waters from these anomalous catchments is their low alkalinity – contents of $\text{HCO}_3^-$ are believed to have mostly been eliminated through buffer reactions. Springs showing low pH in both regions, relative to average pH values from the whole of the area, have enhanced contents of Al and Be. The Al contents in Jizerské hory areas are three times higher while concentrations of Be are doubled. In Krusne hory area the aluminum contents in acidified springs are as much as five times higher relative to springs not affected by acidification.

Table 4. Development of groundwater chemistry in acidified springs (pH < 5.5) during the period 1971-2009 (Krusne hory Mts., average from 11 springs)

<table>
<thead>
<tr>
<th>period</th>
<th>percentage from total number</th>
<th>Na</th>
<th>K</th>
<th>NH$_4^+$</th>
<th>Mg</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Al</th>
<th>Be</th>
<th>Cl</th>
<th>NO$_3^-$</th>
<th>NO$_2^-$</th>
<th>HCO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>F</th>
<th>mineralization</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1971-1975</td>
<td>78%</td>
<td>5,9</td>
<td>2,7</td>
<td>0,01</td>
<td>3,15</td>
<td>13,5</td>
<td>0,0</td>
<td>0,23</td>
<td>?</td>
<td>7,14</td>
<td>1,2</td>
<td>0,0</td>
<td>10,65</td>
<td>40,7</td>
<td>0,09</td>
<td>92,97</td>
<td>5,19</td>
<td></td>
</tr>
<tr>
<td>1983-1987</td>
<td>37%</td>
<td>3,7</td>
<td>1,3</td>
<td>0,06</td>
<td>2,61</td>
<td>10,3</td>
<td>0,17</td>
<td>1,17</td>
<td>1,27</td>
<td>?</td>
<td>3,76</td>
<td>7,6</td>
<td>0,0</td>
<td>1,72</td>
<td>41,4</td>
<td>0,29</td>
<td>76,95</td>
<td>4,62</td>
</tr>
<tr>
<td>1997</td>
<td>57%</td>
<td>3,4</td>
<td>1,1</td>
<td>0,01</td>
<td>?</td>
<td>7,4</td>
<td>0,0</td>
<td>0,5</td>
<td>0,2</td>
<td>0,07</td>
<td>5,20</td>
<td>5,0</td>
<td>0,0</td>
<td>0,0</td>
<td>5,7</td>
<td>19,3</td>
<td>?</td>
<td>62,2</td>
</tr>
<tr>
<td>2008-2009</td>
<td>57%</td>
<td>3,3</td>
<td>1,7</td>
<td>0,03</td>
<td>2,88</td>
<td>10,4</td>
<td>0,60</td>
<td>0,63</td>
<td>0,74</td>
<td>0,07</td>
<td>5,3</td>
<td>4,6</td>
<td>0,0</td>
<td>6,0</td>
<td>33,8</td>
<td>0,19</td>
<td>77,27</td>
<td>4,97</td>
</tr>
<tr>
<td>1971-2009</td>
<td></td>
<td>4,3</td>
<td>1,7</td>
<td>0,03</td>
<td>2,88</td>
<td>10,4</td>
<td>0,60</td>
<td>0,63</td>
<td>0,74</td>
<td>0,07</td>
<td>5,3</td>
<td>4,6</td>
<td>0,0</td>
<td>6,0</td>
<td>33,8</td>
<td>0,19</td>
<td>77,27</td>
<td>4,97</td>
</tr>
</tbody>
</table>

4.2 Impact of forest on groundwater quality

Forest health is in general an essential indicator of environmental conditions. This particularly applies to mountainous regions of the Czech Republic where the forest has gone through dramatic changes during the last few decades. The following analyses and their interpretation were focused on the assessment of relationship between forest health and the quality of ground waters.
This close link can be well demonstrated with the example of Jizerské hory Mts. where detailed analysis showed similar dynamics of evolution of forest health as that recorded in the Krušné hory Mts. (see chapter 2.1.). In 1984, forest health in Jizerské hory Mts was at the worst condition when 20% of conifers and 11% of deciduous trees were in a strongly to very strongly damaged category and more than 50% of conifer forest were in worse condition than the medium damaged category. Since 1984, there has progressively existed a better condition or trend in forest health which until 1997 was subjected to massive felling of sick trees. The areal extent of conifer forest decreased during the period 1984 – 1997 by 30%, while the proportion of deciduous trees increased. Only the next decade is marked by coniferous tree planting of which the area currently slightly exceeds its initial areal extent. Simultaneously, the initial proportion of conifer and deciduous trees returned to the original state.

Trends in the evolution of forest health correspond to changes in the quality of groundwater described in chapter 2.2. The close link between forest health and the quality of ground waters is demonstrated by the following two graphs for a coniferous forest.

The graph shows markedly greater proportion of damaged forest in catchments affected by acidification. An improving trend in forest health towards the end of the 1990s, and on the contrary a worsening of the forest health at the onset of new century correlate with the evolution of pH and concentrations of Al and Be.

Similar conclusions demonstrating a close link between the quality of ground waters and forest health can be drawn from the results obtained in the Krušné hory Mts. The following Table 6 demonstrates the close relationship between forest health and the quality of ground waters in experimental catchments in Krušné hory Mts.

In catchments where the forest showed a low level of damage, the pH of the groundwater was up to half an order higher than in areas showing a greater degree of damage. In catchments with severely damaged forest, the groundwater had enhanced concentrations of aluminum and low alkalinity.
<table>
<thead>
<tr>
<th>Damage degree</th>
<th>Characteristic of the forest</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Health forest</td>
</tr>
<tr>
<td>O/I</td>
<td>First symptoms of damage</td>
</tr>
<tr>
<td>I</td>
<td>Slightly damaged forest</td>
</tr>
<tr>
<td>II</td>
<td>Medium damaged forest</td>
</tr>
<tr>
<td>IIIa</td>
<td>Highly damaged forest</td>
</tr>
<tr>
<td>IIIb-IV</td>
<td>Dead forest</td>
</tr>
</tbody>
</table>

Fig. 12. Comparison of the evolution of coniferous forest health in all experimental catchments in the Jizerské hory Mts (A) and in strongly acidified catchments with pH lower than 5.5 (B).
The behavior of nitrates corresponds with their use as fertilizers. Only relatively healthy forest is able to eliminate the impacts of atmospheric nitrogen. Therefore, the enhanced concentrations of nitrates occur in areas without forest vegetation or in those with heavily damaged forest.

The fact that the mere existence of the forest as such magnifies the effect of atmospheric deposition on the quality of groundwater is demonstrated by comparison of the chemistry of groundwater in catchments differing from one another by forest density. Catchments with areal extent of forest exceeding or smaller than 50% of the total area were mutually compared. As follows from Table 7 the catchments covered with greater proportion of forest are characteristic of higher degree of acidification, have lower contents of HCO₃, lower pH and enhanced contents of Be, Al and sulfates. Forested catchments in Krušné hory Mts. as well as in Jizerské hory Mts. are low in nitrates. In this particular case the forest plays a positive role because it uses nitrogen from atmospheric deposition as a fertilizer. Anthropogenic deposition of nitrogen is directly linked with greater forest growth (Kaupi et al. 1992, Binkley and Hogberg 1997, Aamlid et al. 2000).

Table 6. Relationship between mean values of major indicators of groundwater acidification and the state of health of the forest in Krusne hory catchments

<table>
<thead>
<tr>
<th>pH</th>
<th>NO₃</th>
<th>HCO₃</th>
<th>Al</th>
<th>Harm category</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.37</td>
<td>7.07</td>
<td>8.33</td>
<td>0.40</td>
<td>IIIa + IIIb IV</td>
</tr>
<tr>
<td>5.68</td>
<td>3.18</td>
<td>9.86</td>
<td>0.20</td>
<td>I - II</td>
</tr>
<tr>
<td>5.82</td>
<td>3.45</td>
<td>19.87</td>
<td>0.20</td>
<td>O+ O/I</td>
</tr>
<tr>
<td>5.86</td>
<td>8.40</td>
<td>16.13</td>
<td>0.10</td>
<td>No forest</td>
</tr>
</tbody>
</table>

Table 7. Comparison of groundwater chemistry in dense and sporadic forested catchment area

<table>
<thead>
<tr>
<th>Area</th>
<th>Percentage of forest from total surface</th>
<th>Na</th>
<th>K</th>
<th>NH₄</th>
<th>Mg</th>
<th>Ca</th>
<th>Al</th>
<th>Be</th>
<th>Cl</th>
<th>NO₃</th>
<th>HCO₃</th>
<th>SO₄</th>
<th>mineralization</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Krusne hory Mts.</td>
<td>to 50%</td>
<td>5.8</td>
<td>2.1</td>
<td>0.03</td>
<td>4.4</td>
<td>14.0</td>
<td>0.19</td>
<td>0.029</td>
<td>7.2</td>
<td>6.2</td>
<td>12.6</td>
<td>39.8</td>
<td>82.4</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>above 50%</td>
<td>4.9</td>
<td>0.7</td>
<td>0.04</td>
<td>2.6</td>
<td>9.16</td>
<td>0.25</td>
<td>0.075</td>
<td>7.1</td>
<td>2.2</td>
<td>6.9</td>
<td>36.8</td>
<td>60.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Jizerské hory Mts.</td>
<td>to 50%</td>
<td>5.6</td>
<td>2.0</td>
<td>0.1</td>
<td>4.1</td>
<td>15.5</td>
<td>0.11</td>
<td>0.032</td>
<td>5.9</td>
<td>11.0</td>
<td>41.5</td>
<td>23.8</td>
<td>142.2</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>above 50%</td>
<td>5.2</td>
<td>1.5</td>
<td>0.1</td>
<td>2.3</td>
<td>11.8</td>
<td>0.42</td>
<td>0.077</td>
<td>6.3</td>
<td>7.2</td>
<td>13.4</td>
<td>27.0</td>
<td>91.0</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Further analysis was focused on the assessment of groundwater quality in the regions with damaged forests. Two types of data were compared: catchments where at least 20% of total surface fall in category highly damaged forest and areas where this criterium was not achieved.

The most conspicuous difference between the two data sets compared from both the Krušné hory and Jizerské hory regions are significantly higher concentrations of Al and Be in catchments with damaged forest.
Groundwater Quality Development in Area Suffering from Long Term Impact of Acid Atmospheric Deposition – The Role of Forest Cover in Czech Republic Case Study

<table>
<thead>
<tr>
<th>area</th>
<th>forest health status</th>
<th>Na</th>
<th>K</th>
<th>NH₄</th>
<th>Mg</th>
<th>Ca</th>
<th>Al</th>
<th>Be</th>
<th>Cl</th>
<th>NO₃</th>
<th>HCO₃</th>
<th>SO₄</th>
<th>mineralization</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/l</td>
<td>μg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Krusne hory Mts.</td>
<td>damaged</td>
<td>3.9</td>
<td>1.5</td>
<td>0.01</td>
<td>4.1</td>
<td>8.8</td>
<td>0.34</td>
<td>0.042</td>
<td>4.4</td>
<td>5.8</td>
<td>7.1</td>
<td>29.3</td>
<td>64.2</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>health</td>
<td>3.7</td>
<td>1.3</td>
<td>0.01</td>
<td>1.2</td>
<td>7.8</td>
<td>0.02</td>
<td>0.021</td>
<td>4.4</td>
<td>2.2</td>
<td>7.7</td>
<td>20.3</td>
<td>51.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Jizerske hory Mts.</td>
<td>damaged</td>
<td>3.1</td>
<td>0.6</td>
<td>0.07</td>
<td>0.9</td>
<td>5.8</td>
<td>0.58</td>
<td>0.108</td>
<td>2.0</td>
<td>3.0</td>
<td>7.7</td>
<td>15.2</td>
<td>49.4</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>health</td>
<td>5.4</td>
<td>1.5</td>
<td>0.04</td>
<td>2.8</td>
<td>14.1</td>
<td>0.29</td>
<td>0.048</td>
<td>6.1</td>
<td>7.3</td>
<td>16.9</td>
<td>32.1</td>
<td>93.5</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Table 8. Comparison of groundwater chemistry in damaged and health forest catchment area

This analysis raises a question of what is the cause and what is the consequence of such a situation? The primary cause is clear – acid atmospheric deposition that obviously worsened the quality of groundwater which in areas covered by damaged forest exhibits high concentrations of Al and Be and low pH. On the other hand, the forest at the same time intensifies the negative effect of atmospheric deposition.

A paradoxical result can be observed at first glance both in the Krušné hory and Jizerské hory regions when catchments with dead or strongly damaged forest show SO₄ and NO₃ concentrations, the major groundwater components, are lower than in the areas with healthy vegetation cover. This phenomenon can be explained by the reduction of the area (needles and leaves) that can catch the dry atmospheric deposition. Consequently, the dead forest does not play its negative role in intensification of the effect of atmospheric deposition on the quality of groundwater.

A similar approach to the assessment of the relationship between the forest cover and quality of ground waters made in the Krušné hory and Jizerské hory regions turned out to be less applicable in the Krkonoše Mts. because of rather poor results. The first reason appears to be the unsuitable selection of monitored catchments. The monitoring grid was established in the 1970s having been merely aimed at monitoring the quality of ground waters. Although the distribution of sampling sites was suited to hydrogeological requirements, the majority of monitored catchments were not forested or the composition and quality of the forest did not characterize natural conditions of this mountain range. The change in the distribution of monitored objects could eliminate this problem, but on the other hand the unique hydro-chemical data acquired in the past could not be used.

The topography of the Krkonoše Mts. is another phenomenon which is different from other regions. Significantly higher altitude (on average 1 000 m a.s.l.) in the Krkonoše Mts. at which 45% of monitored catchments are located, while in the Jizerské hory region only one catchment lies above 1 000 m a.s.l. and in the Krušné hory area all monitored springs lie at altitudes below 900 m a.s.l. Consequently, the set of hydrochemical data in Krkonoše Mts characterized mostly an environment without any forest or its proportion in relation to total area was small and mostly did not exceed 25%.

The chemistry of ground waters in the Krkonoše Mts differs more or less significantly from that in the Krušné hory and Jizerské hory regions which could have been due to a very small number of samples collected in forested catchments. So, the current better quality of ground waters in the Krkonoše Mts. can be influenced, besides the primary cause which is their shorter exposure to acid atmospheric deposition, by prevailing tundra with dwarf pine...
covering the apical parts of the mountain range. This environment must have had limited ability to catch dry deposition in relation to the grown forest, and the bulk deposition was mostly responsible for acidification in the Krkonoše Mts.

5. Conclusion

A comparison of the evolution of groundwater chemistry in three mountain regions of the Czech Republic shows that dramatic changes have taken place during approximately the last 50 years. The regional interpretation of hydrochemical data was based on the assumption that the chemical composition of ground waters at all the localities studied was more or less the same and corresponded to natural background during the period prior to the impact of anthropogenic activities. This assumption was justified by the fact that the geology underlying all three regions investigated is more or less the same. The bedrocks are chiefly metamorphic rocks intruded by granites. The topography and climate of the three regions are similar and until the 1960s the land was covered by spruce monocultures, which gradually became extinct due to acid precipitation.

The results of the investigation revealed that long-term acid precipitation from the atmosphere had a markedly detrimental effect on the quality of local ground waters. The changes common to all regions were the decreases in pH and alkalinity and increases in the contents of SO$_4^{2-}$, Al and Be. However, the intensity of these changes varied considerably from one region to another. The period of time during which the regions became subject to the negative effects of anthropogenic activity has been shown to play a decisive role in changes of groundwater chemistry.

The greatest changes in the quality of groundwater, that have persisted until today, occurred in the Krušné hory Mountains where acid atmospheric deposition has taken place more or less continuously for almost a hundred years, peaking in the 1960s and 1970s. The initial Ca-HCO$_3^-$ type of groundwater formerly found in the Krušné hory region has clearly been changed to groundwater of Ca-SO$_4^-$ type containing a concentration of sulfates five times more than that of the HCO$_3^-$ component.

Acid atmospheric deposition in the Jizerské hory and Krkonoše Mountains has taken place only for about 25 years. The groundwater chemistry showed the same trend as in the Krušné hory region but to a much lower extent. Moreover, the Krkonoše area also revealed that these hydrochemical changes are not irreversible because the chemistry of ground waters during the last few years is gradually returning to the preexisting Ca-HCO$_3^-$ type.

In contrast, it is believed that the return of groundwater chemistry in the Krušné hory region to the initial quality will take a much longer period of time. Although the problem of acid atmospheric deposition of sulfur has been successfully resolved, the prolonged accumulation of sulfur in the soil profile has created a persistent secondary source of this element that still affects the quality of local ground waters.

The quality of the ground waters in the three regions investigated showed significant heterogeneities and anomalies. Detailed analysis of the factors influencing the quality of ground waters affected by acid atmospheric deposition revealed the significant negative role played by coniferous monocultures in groundwater chemistry. The negative impact of acid deposition on the quality of groundwater in the majority of cases was found to have been more intense in areas covered by forest. This was best demonstrated in the case of spruce...
forest that has a much greater capacity to trap dry atmospheric deposition in the form of
dust particles and aerosols. Forest catchments more often revealed anomalous
concentrations of toxic aluminum and/or beryllium. The other aspect of this phenomenon is
that the deterioration of ground water quality caused by the forest in turn affects the health
of the forest itself. Damaged or completely dead forest was found to occur most frequently
in catchments showing high degrees of acidification.

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The book attempts to cover the main fields of water quality issues presenting case studies in various countries concerning the physicochemical characteristics of surface and groundwaters and possible pollution sources as well as methods and tools for the evaluation of water quality status. This book is divided into two sections: Statistical Analysis of Water Quality Data; Water Quality Monitoring Studies.

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