

## Mapping Critical Loads/ Exceedances: Natural Waters of Slovakia

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### Abstract:

Acidification of natural water due to acid precipitation is an environmental problem affecting large areas of Europe and eastern regions of Northern America. Acidification is causing ecological changes of natural environment and fish mortality. Within the contract on environmental co-operation between Norway and Slovakia, this contribution presents results of the pilot stage of the project "Mapping critical levels/loads for Slovakia", realised in the central part of Slovakia (map sheet 1 : 200 000 Banská Bystrica), in a 10 x 10 km grid. Critical loads were calculated from the present chemical composition of surface and groundwater with the help of steady-state model (SSWC). Critical loads of acidity for surface water were systematically higher than those for groundwater. Acidity values have not been exceeded in surface, neither in groundwater in any of the cells.

*Key words:* critical loads/exceedances, surface water streams, groundwater, steady-state model

5 figs.

### 1. Introduction

Solving of the problems of impact of acid deposition on different components of natural environment is a serious scientific as well as political interest in many countries of Europe and Northern America. The most important for the evaluation of the effects of strong acids from atmospheric deposition on natural water, forests, soils, the condition of biotop, human health and various materials (cultural monuments etc.) is the determination and definition of limits for the deposition of acid components. These limits or critical loads are defined as "highest depositions of acid components causing no changes leading to long-term harmful effects on the

structure and function of an ecosystem" (NILSSON-GRENUFELT, 1988). The aim of determining and defining critical loads is to determine the quantity and character of acid component deposition (above all SO<sub>x</sub>, NO<sub>x</sub>, organic compounds etc.) in a way that would protect the environment in the future. On the basis of the "Convention on Long-Range Transboundary Air Pollution" (the Geneva convention), "Task Forces for Mapping the Critical Loads and Areas where the Critical Loads are Exceeded" have been formulated. The manual for calculating critical loads and their exceedances for soils as well as surface water, has been elaborated by SVERDRUP et al. (1990). In Scandinavian countries (Finland, Sweden and Norway), critical loads and their exceedances have been calculated on the basis of regional data on chemical composition of surface streams in an EMEP grid (150 x 150 km), divided into 3 and 3 sub-parts (HENRIKSEN et al., 1992).

The Slovak Republic came into existence at the beginning of 1993, after the disintegration of the Czechoslovak Federal Republic. The project of critical loads mapping became stagnant. For this reason, as a part on the Agreement on Environmental Co-operation between Norway and Slovakia, the project "Mapping Critical Levels/Loads for Slovakia" was launched in 1992, with participants from the Norwegian Institute for Water Research (NIVA), the Lund University, the Slovak Hydrometeorological Institute, the Dionýz Štúr Institute of Geology in Bratislava, the Forest Research Institute in Zvolen, the Forestry University in Zvolen and Research Institute for Irrigation in Bratislava.

The realisation of the project started in June 1994. The contribution presents results of mapping of critical loads and their exceedances in natural



(ground- and surface) water from a selected pilot region (map sheet 1 : 200 000 Banská Bystrica), representing approximately 20% of the Slovak territory.

Grid size for the construction of critical loads map of Slovakia corresponds to the EMEP grid. The EMEP grid cell of 50x50 was subdivided into 25 cells. This means that the grid distance was approximately 10 km.

Critical acidity loads were calculated on the basis of present chemical composition of ground- and surface water. In the contribution there is presented the method used for the evaluation of critical loads for natural water, while we assumed sulphur was the only acidifying component. We are considering to include in future into the calculations also another important acidifying component - nitrogen.

## 2. Natural conditions of the pilot territory

The pilot area represents about 20% of the total Slovak territory. It includes the following geographic units: In the northern part, from west to east: Malá Fatra Mts. (highest peak 1574 m a.s.l.) and the Nízke Tatry (Low Tatras) Mts. (highest peak Ďumbier 2043 m a.s.l. - the highest point of the area). In the southern part, from west to east - Štiavnické vrchy Hills (highest peak 1009 m a.s.l.), Kremnické vrchy Mts. (highest peak 1265 m a.s.l.), Javorie (highest peak 1044 m a.s.l.), Poľana (highest peak 1458 m a.s.l.), Veporské vrchy Hills (highest peak 1439 m a.s.l.) and in the south-eastern part the Revúcka pahorkatina Hills (highest peak 602 m a.s.l.). The lowermost location in the south-eastern part of the pilot area is only 200 m high above sea level.

The largest part of this territory belongs to the drainage area of the river Hron. Northern slopes of the Nízke Tatry Mts. are drained by the river Váh and the south-eastern part of the area belongs to the drainage area of the river Ipel.

The geological structure of the area under study is composed of practically all most important geological units forming the Western Carpathians. From geological point of view, mountainous areas of this region may be divided as follows:

- I. region of core mountain ranges
- II. region of Central Slovak Neovolcanics

The lowlands may be divided into:

- III. intramontane depressions
- IV. alluvial deposits or large rivers

I. Core mountain region - the Nízke Tatry Mts., Malá Fatra Mts., Veľká Fatra, Slovenské Rudohorie - are in their central part underlain by various granites, granodiorites and gneisses and, to a lesser extent, by amphibolites. Marginal parts of the above mountain ranges have as their basement Mesozoic, mainly carbonate rocks, lying in cover or nappe position:

- limestones
- dolomites
- marls and marly limestones

II. Central Slovak Neovolcanic region - Štiavnické vrchy and Kremnické vrchy Hills are composed of differed varieties of neovolcanic rocks, mainly andesites, rhyolites and their tuffs.

III. Intramontane depressions - underlain mostly by Tertiary sediments - gravels, sands, clays, sandstones and claystones.

IV. Alluvial deposits of large rivers - the rivers Váh and Hron and their tributaries are underlain predominantly by gravels and sands.

All grids are fully or partially covered with forests. There are three main forest areas (spruce, beech and oak) on the pilot territory.

## 3. Data used for map construction

An important part of the project was the selection of data, constituting the input into the calculation scheme, as well as their adjustment. The representing and information capacity of thus obtained values is at the same time indicative of the quality of existing databases at SHMÚ and GÚDŠ.

### 3.1 Atmospheric precipitation, deposition and hydrogeologic conditions

The distribution of atmospheric precipitation and hydrologic characteristics on the pilot area is considerably affected by its extraordinary variability. Average altitudes a.s.l. of the grid cells occur in the range of 250 m in the south-eastern part of the pilot area up to 2043 m in the cell crossed by the crest of Nízke Tatry Mts. Altitude differences in the grid cells



often exceed 500 m, in some cases even 1000m. We must bear this in mind when interpreting all average values related to the cells.

Average total annual precipitation in the grid cells have been determined from isohyet map of 30 annual precipitation (1961–1990). This map has been elaborated by the department of climatology at Slovak Hydrometeorological Institute (SHMÚ), on the basis of results obtained from measurements at 116 precipitation stations. The density of the precipitation-measuring network is irregular and decreases with increasing altitude above sea level. It is necessary to stress that the measurement of precipitation in mountain drainage areas, especially in winter, are loaded with a systematic negative error, which in the crest areas of the Nízke Tatry Mts. can exceed 40% of the listed value. The magnitude of the error is a function of the degree of exposure of the station, its determination is difficult and it is possible only by special measurements. Data of precipitation stations are thus presented without correction. In medium-high locations (600–1200 m) the magnitude of the correction in exposed sites is 25–30%, at protected locations it is less than 20%.

Average annual total precipitation on the pilot territory were the lowest (500–650 mm) in its south-eastern part and the highest (1400–1500 mm) on the crest of the Nízke Tatry Mts.

The concentration of sulphates in precipitation water on the whole Slovak territory is a relatively conservative characteristic. Its low horizontal gradient is directed from the north-west to the south-east of the country. Average annual concentration of sulphates in precipitation water in the studied territory in the last five years (1989–1993) was 1.8 mg S/l. In comparison with the first half of the eighties, the present concentration is by about 30% lower, which is consistent with the European decrease of sulphur dioxide emissions.

The bulk deposition of sulphur consists of three components: wet, dry and hidden. The wet deposition may be determined relatively simply on the basis of the results of chemical analysis of precipitation as the product of concentration in precipitation water and total precipitation. Wet deposition of sulphur increases with altitude. Average wet deposition of sulphur in the grid cells in the relevant period varies within the range of 0.6 to 1.8 keq/ha/year.

Average annual  $\text{SO}_2$  concentration on the crest of the Nízke Tatry Mts. was in the last years 4–5

$\mu\text{g}\cdot\text{m}^{-3}$ . In valleys (outside cities) they were about three times higher. Assuming an average rate of dry  $\text{SO}_2$  deposition of 0.7 cm/s, the dry deposition of sulphur in high mountain levels represents only 10–20% of wet deposition. We may assume a ratio of 1 : 1 for wet and dry deposition in valleys.

Hidden sulphur deposition (capture of water from clouds and fogs on the surface, especially by vegetation) increases with altitude and in higher mountain levels, in relation to their degree of exposure, it may become equal to or even exceed wet deposition. In valleys of the studied territory the contribution of hidden sulphur deposition decreases below 20% of wet deposition.

In view of the absence of measurements of dry and hidden deposition, the bulk deposition of sulphur is estimated in the presented work as twice the wet deposition. This value results from the above considerations and it represents a conservative estimate of the real deposition of sulphur on the pilot territory.

The same factor has been used also in the calculation of total deposition of base cations (Ca, Mg). The uncertainty of this factor is nevertheless considerably higher in comparison with sulphur. Average annual Mg concentrations in precipitation water varied in the range of 0.1–0.3 mg/l, in the case of Ca they were two to three times higher. Total deposition of base cations in equivalent quantities in all cells of the relevant grid represents approximately the half of total sulphur deposition.

Hydrogeologic conditions of the pilot territory are reflecting also its relatively complex geological-geomorphologic setting. From this viewpoint the selected region contains territorial units representing lower regions up to high mountains. A considerable part of the area belongs to a headwater region with sources of good-quality drinking water. The selection of hydrological characteristics was determined by the methodology of the pilot project.

Generally it can be said that the increase of precipitation and decrease of evaporation lead also to increased run-off. Therefore in the Western Carpathians average specific annual run-off increases with altitude and decreases with increasing surface of drainage area. The cells from the viewpoint of preservation of the drainage basin as a natural hydrological unit are not consistent with this. In some cases they contain two or three drainage basins and the determination of sufficiently representative hydrological characteristics is quite difficult.



The derivation of specific run-off was based on isoline map of elementary run-offs and corresponding run-off levels. SHMÚ has these data in its database and isoline maps of elementary run-off are representing the evaluated 50-year data material as basic information for the expertise of this institute. The variability of specific run-off is considerable and its values vary in the range of 2 l/s.km<sup>2</sup> (lowlands) up to 45 l/s.km<sup>2</sup> (in mountainous regions). Specific run-off for each cell was determined as weighted average from the relevant area and calculated run-off level. This value, given as m<sup>3</sup>/year, is another input into the SSWC stationary model and it represents the run-off level for the relevant cell.

Values of run-off level are considerably variable and they are representing the natural condition of each cell. Their values vary in the range of 0.98–0.7 m<sup>3</sup>/year for the Nízke Tatry Mts. region, 0.6–0.4 m<sup>3</sup>/year for the intramontane region. Lower situated parts, such as the south-eastern part of the map sheet, have values of 0.2–0.09 m<sup>3</sup>/year.

### 3.2 Chemical composition of natural waters

Input data for the chemical composition of groundwater represented a selection from the GÚDŠ database, containing 16 391 chemical analyses from one-specimen sampling of the whole Slovak territory, carried out in the years 1991–1993 with the aim of compiling the Geochemical Atlas of Slovakia - part groundwater. Sampling density was 1 sample/3 km<sup>2</sup>. Sampling sites were predominantly springs, shallow drillholes, wells and outflow from mining works, i.e. the collected information shows the distribution of determined components in the first water bearing horizon.

For the calculation of critical loads, average values of selected components have been calculated for the 10x10 km grid cells, from those sampling sites occurring in the relevant grid cell, which was in average 3 sampling sites.

The most frequently represented in the pilot area are groundwaters of Ca(Mg)-HCO<sub>3</sub> type, with frequent transition to the Ca-SO<sub>4</sub> chemical type. The relatively frequent presence of water of various transitional and mixed types is related to the effects of specific genetic factors (simultaneous effects of several mineralisation factors in the water-bearing aquifer, mixing of waters of various origin etc.) and to locally important effects of anthropogenic factors.

Total dissolved solids of groundwater varies mostly in the range 0.05–1.0 g/l, locally it attains 5 g/l.

The source of base cations (Ca, Mg) are interaction processes water-rock, the most extensively occurring ones in the pilot area being the dissolution of carbonates and ion-exchange processes.

The source of data for the chemical composition of surface stream water were data from the SHMÚ monitoring network and one-specimen sampling carried out by GÚDŠ for the project "Investigation of geological factors of the environment – a perspective programme of Slovak geology" (VRANA, 1992).

Predominant elements in the chemical composition of surface water are calcium and magnesium as products of chemical weathering of rocks, other cations are present in lesser quantities, which is related to the effects of groundwaters and local anthropogenic contamination. From anions, hydrogen-carbonates are predominant, but in many cases there are substantially represented also sulphates, due to effects of mine waters, or tectonic dissemination of Ca-SO<sub>4</sub> waters from underlying carbonates (sulphate concentrations reach locally 100–500 mg/l). In the upper sections of surface streams is the chemical composition approximately the same.

### 4. Calculation method

The definition of critical load is the basis for the calculation or estimation of loads with negative effects.

**Critical load:** the highest load that does not lead to long-term harmful effects on biological systems, such as forest decline or decline and disappearance of fish populations.

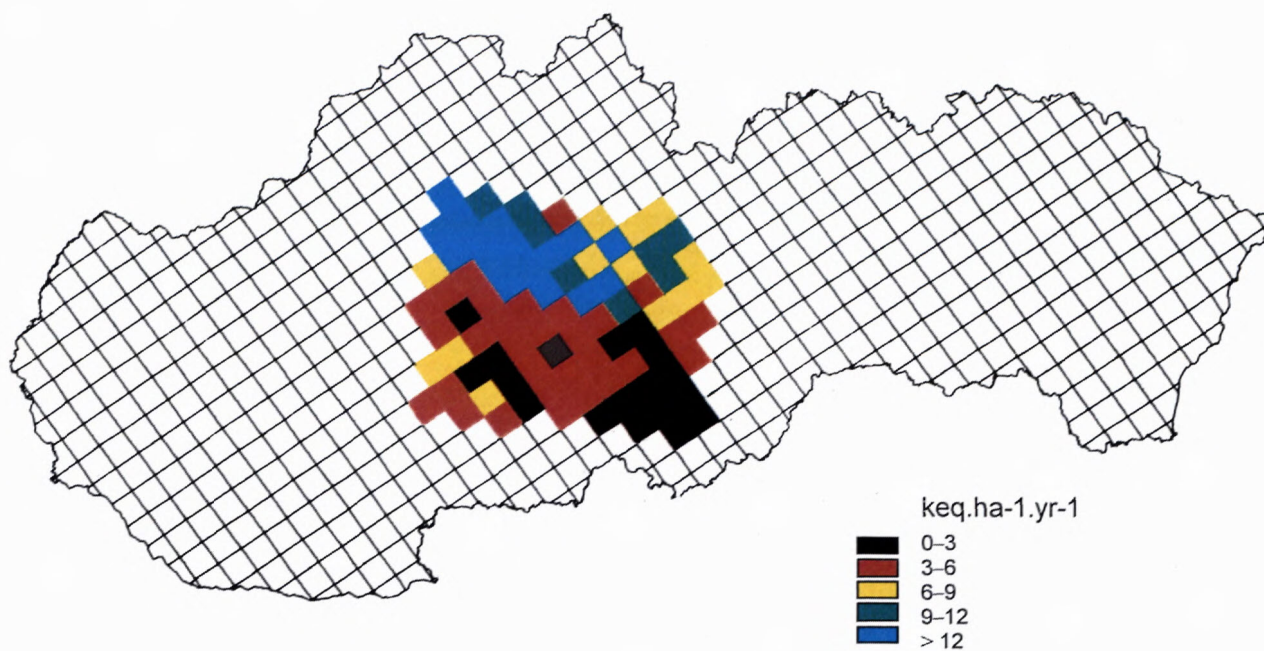
**Receptor:** An ecosystem which may be potentially affected by atmospheric input of sulphur and nitrogen (soil, groundwater, surface water).

**Biological indicator:** Selected organism(s) or populations which are sensitive to chemical changes resulting from atmospheric input of sulphur and nitrogen (forest, fish, invertebrates).

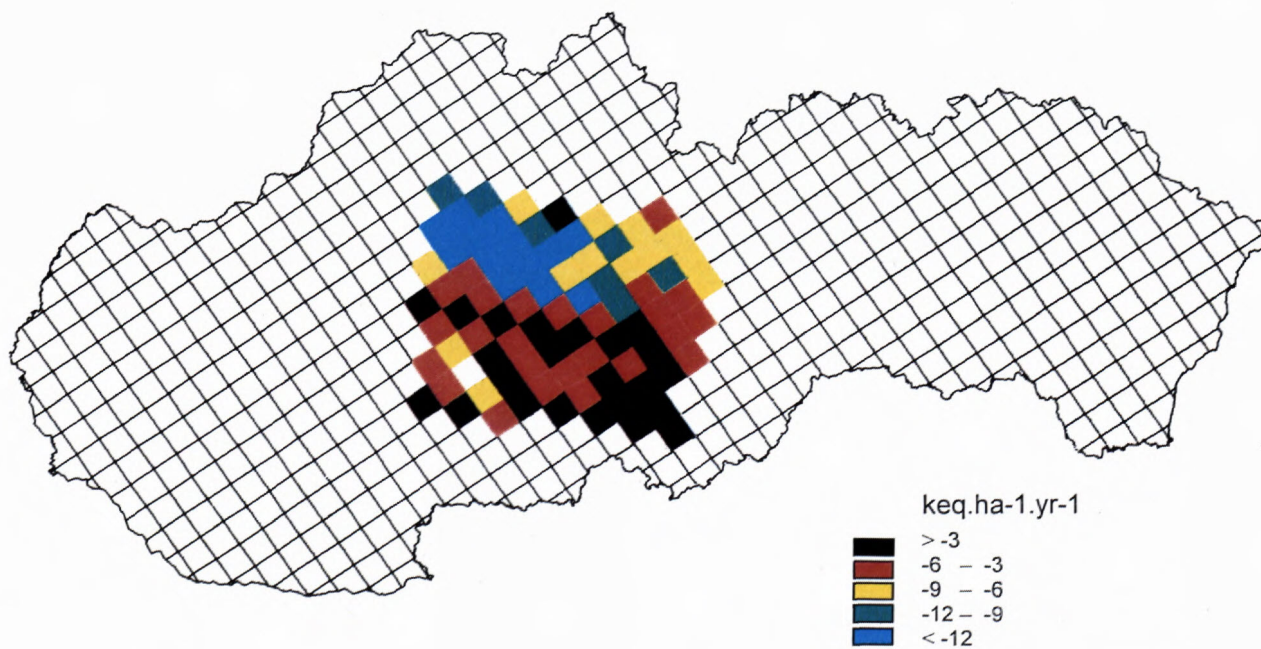
**Critical chemical value:** The value of a critical chemical component or combination of components (pH, ANC, Al/Ca) above or below which there are no harmful effects to the biological indicator. Acid neutralising capacity (ANC) is the ability of a solution to neutralise the inputs of strong acids to a pre-



**SLOVAK REPUBLIC**  
**Critical Loads of Acidity**  
 Receptor: Surface Water

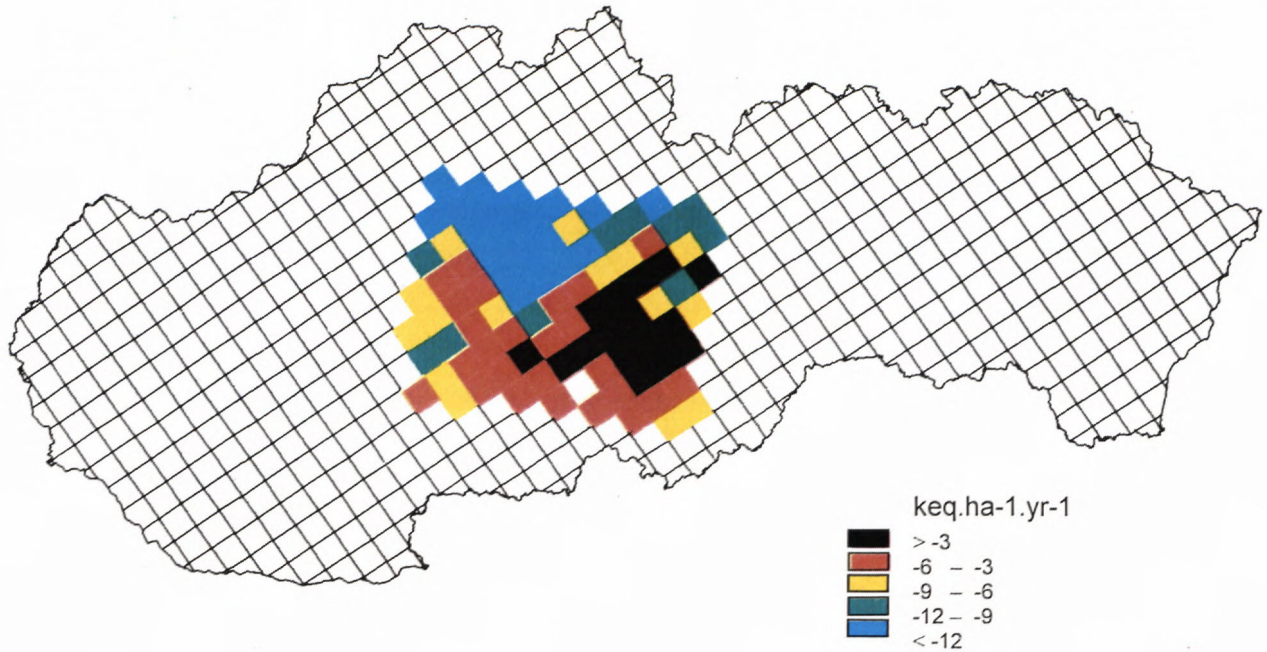


**SLOVAK REPUBLIC**  
**Exceedance of Critical Loads of Acidity**  
 Receptor: Surface Water

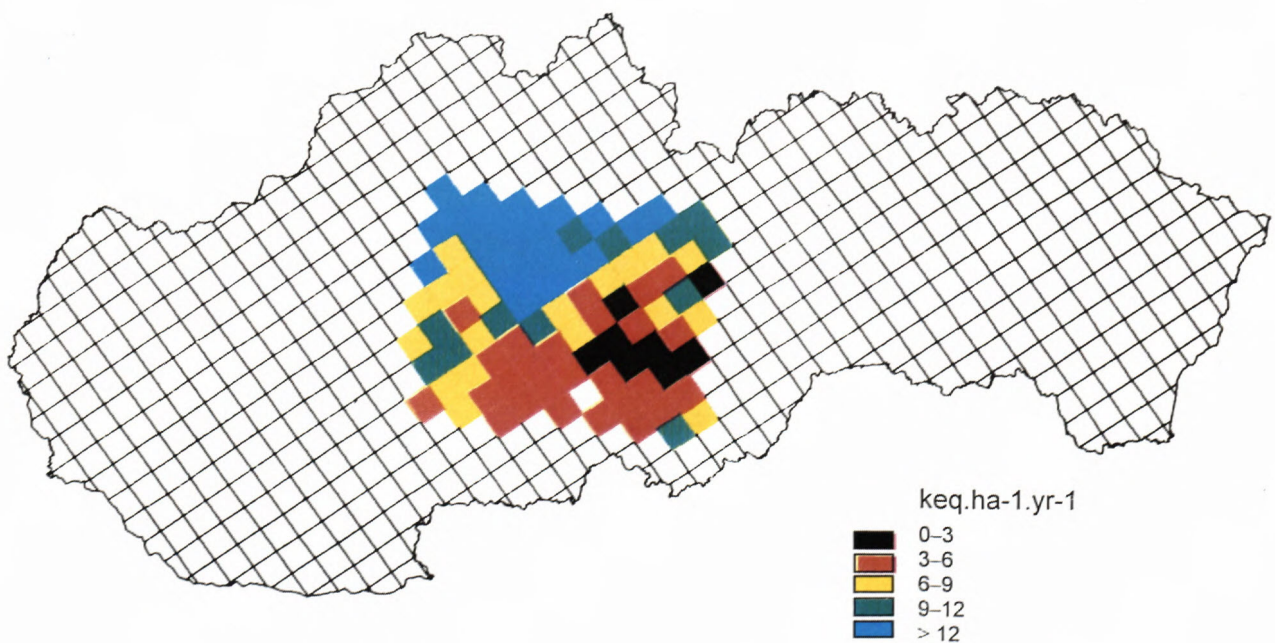




**SLOVAK REPUBLIC**  
**Exceedance of Critical Loads of Acidity**  
**Receptor: Ground Water**



**SLOVAK REPUBLIC**  
**Critical Loads of Acidity**  
**Receptor: Ground Water**





selected equivalence. For surface water, ANC has been selected as the critical chemical value and it has been set relative to fish as the biological indicator. ANC is thus the critical concentration for fish. The use of ANC is a simplified approach, in which numerous interacting factors affecting the toxicity to fish, including pH, aluminium and TOC, are grouped into a single variable. Data on water chemistry and general change of fish status have been used in Norway for assessing the ANC for fish. Few fish populations are damaged at ANC concentrations above 20 meq/l. Of the fish species studied, salmon, brown trout and roach were the most sensitive and perch the least sensitive. Although ANC will depend on fish species considered, a value of 20 meq/l seems to be appropriate for the evaluation of critical loads and critical load exceedance for freshwater fish, at least in Norway. Canada has set pH 6.0 (corresponding to an ANC range of 20-40 meq/l for freshwater lakes) as an appropriate chemical threshold used for defining critical loads, disregarding areas with historical pH values below 6.0. This level has been set to protect all aquatic biota. Sweden is using pH > 6.0 and ANC = 50 meq/l as the national threshold value.

The basic steady state surface water chemistry method (SSWC) is based on the fact that sulphates found in surface water originate largely from sea salt spray and polluted deposition and in the method there are ways of correction for sea salt and minor contribution from geological sources, allowing to obtain atmospheric contribution of sulphate in the water (HENRIKSEN et al., 1988, 1990). This sulphate concentration is then used to obtain the weathering rate of the catchment. The chemical data from the pilot area indicate that the geology supplies a significant amount of sulphate to the water. This sulphate is assumed to be balanced largely by base cations BC (Ca+Mg). Thus, to calculate the critical load, the method must be modified. The atmospheric sulphate contributed to surface and groundwater is estimated by multiplying the sulphur deposition by the ratio of precipitation to run-off. The difference between this value and the sulphate concentration is then geologically supplied sulphate. Since this component is balanced by Ca+Mg, this amount must be deduced from the concentration of base cations to obtain those resulting from weathering and ion-exchange processes. To estimate the ion exchange base cations, a modified F-factor has

been used because of the very high weathering rate in the surface and ground water. Ignoring nitrate concentration, the following calculation method results:

$$SO_{4\text{ dep}} = S_{\text{dep}} \times P/Q$$

where

$S_{\text{dep}}$  = present sulphur deposition in keq/km<sup>2</sup>/year

P = annual precipitation in mm

Q = annual run-off in m<sup>3</sup>

$$BC_{\text{geol}} = SO_{4\text{ r}} - SO_{4\text{ dep}}$$

where

$BC_{\text{geol}}$  = base cations of geological origin

$SO_{4\text{ r}}$  = sulphate concentration in run-off water

$$BC_{\text{wt}} = BC_{\text{t}} - BC_{\text{geol}}$$

where

$BC_{\text{wt}}$  = present weathering rate

$BC_{\text{t}}$  = present Ca+Mg concentration in run-off water

The F-factor is defined as the change in base cation concentration due to a change in the concentration of sulphate

$$F = BC_{\text{wt}}/S$$

where

S = base cation concentration at which F=1. The value of 4 meq/l for S has been used in this report

Then: 
$$BC_{\text{w}} = BC_{\text{wt}} - F \times SO_{4\text{ dep}}$$

The critical loads of acidity (CL) and critical load exceedance (CL-Ex) are then given:

$$CL = BC_{\text{w}} \times Q \times 10 \text{ (keq/ha/year)}$$

$$CL\text{-Ex} = S_{\text{dep}} - CL \text{ (keq/ha/year)}$$

## 5. Discussion and conclusions

Results of the calculation of critical loads and exceedances for the acidity of ground- and surface waters for the pilot area of Slovakia is represented on Figs. 1, 2, 3, 4. The colour and value ranges are adjusted to be consistent with international presentations of critical loads.

From the viewpoint of critical loads of acidity the values of surface waters were systematically higher than those for groundwater at correlation of 0.69 (Fig.5).



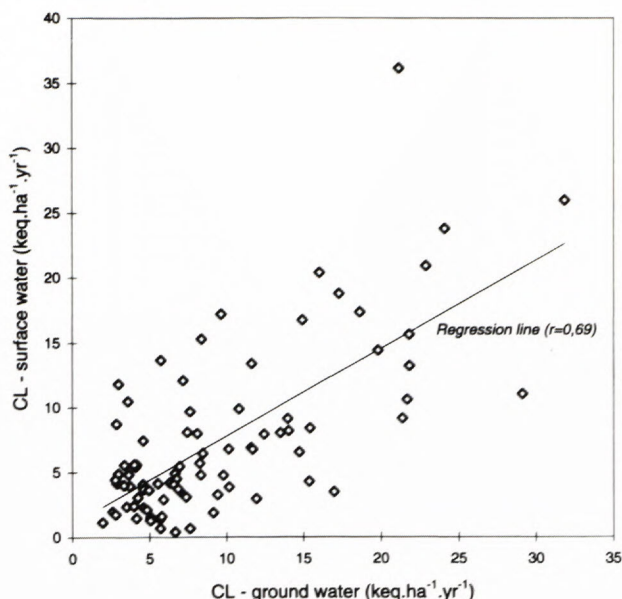


Fig. 5 Relationship between critical loads of ground waters and surface waters

The calculated exceedance values at both receptors display high negative values in the greatest part of the pilot area, i.e. they indicate that there are reserves for further contributions of acid deposition. This situation is related to the time of water sampling in the studied territory, i.e. it does not record changes in the chemical composition in time and thus it does not allow to make a prognose. The calculated critical loads reflect in practice the conditions in which chemical composition of water formed, especially geological setting of the territory and hydrodynamic conditions of circulation. The locally higher sensitivity has been caused by outflow from mine works and dispersion of groundwater from the underlier into surface streams. The generally higher sensitivity of the southern part of the

pilot area is probably caused by lower velocity of groundwater flow and an important factor is also anthropogenic contamination.

The critical loads and exceedance calculation for natural water presented in the contribution are the first application of this environmental technique in Slovakia. A simple steady-state model (SSWC) has been used, including only sulphur. In the next stage, critical loads of natural water will be calculated in a 10x10 km grid for all Slovakia.

*Acknowledgements:* The authors would like to express their gratitude to Mr. Arne Henriksen and Mrs. Bente M. Wathne from the Norwegian Institute for Water Research (NIVA), for their introduction to the problem of critical loads/exceedances calculation and consultations to the above problems.

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