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WATER POLLUTION ABATEMENT PROGRAMME
THE CZECH REPUBLIC

PROJECT 4.2

ASSESSING CRITICAL LOADS OF ACIDITY TO SURFACE
WATERS IN THE CZECH REPUBLIC

**Critical loads of acidity to surface waters
Northern Moravia and Silesia,
The Czech Republic**

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Abstract: Critical load of acidity to surface waters and exceedance of critical load were estimated for northern Moravia and Silesia in The Czech Republic. High critical loads were calculated for the examined region. Critical loads for soils are lower than those for surface waters in parts of the examined region. No area of the examined region showed exceedance of critical load for surface waters. The studies will continue in northern Bohemia in 1994.

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WATER POLLUTION ABATEMENT PROGRAMME. THE CZECH REPUBLIC

Project 4.2
Assessing critical loads of acidity to surface waters in The Czech Republic

CRITICAL LOADS OF ACIDITY TO SURFACE WATERS

NORTHERN MORAVIA AND SILESIA,

THE CZECH REPUBLIC

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PREFACE

The Governments of Norway and Czech and Slovak Federal Republic have signed a bilateral environmental protection agreement. As part of this agreement several collaborative projects were identified. The Norwegian - Czechoslovak working group for the protection of the environment decided to contract Norwegian Institute for Water Research (NIVA) in co-operation with the Water Research Institute (WRI), Prague, Institute of Industrial Landscape Ecology (IILE), Ostrava , Mining University, Ostrava (MUO), and Povodi Odry (PO) to execute several projects under the programme area "Abatement strategies in the River Odra catchment".

As part of the project, a group of scientists from The Czech Republic visited Oslo in October 1992. During the visit a new project was proposed: "Assessing critical loads of acidity to surface waters in The Czech Republic." The project started in the region of northern Moravia in 1993, and it was supported by a grant from The Ministry of Environment of The Czech Republic in 1993. The project is a co-operation of the Norwegian Institute for Water Research (NIVA) and the Mining University, Ostrava (MUO).

The present report is a translated and revised version of the Czech report: "Mapovani kritických zateží v povrchových vodách" (Mapping of critical load of surface waters) prepared by Raclavský et al. 1993.

Oslo, April 1994.

Leif Lien

CONTENTS	page
Preface	3
Summary	5
1. Introduction	6
2. Definitions	7
3. Calculating critical loads of acidity to freshwater	7
4. Description of the sampling area: Northern Moravia and Silesia	9
4.1 Location of the study area	9
4.2 Geological composition of the area	12
4.3 Climatological conditions	12
4.4 Soil	15
4.5 Vegetation	15
5. Material and methods	16
5.1 Seasonal variations of element concentrations in surface waters	16
5.2 Sampling	16
5.3 Chemical analyses	19
6. Critical loads of Northern Moravia and Silesia	19
7. Maps of critical load and exceedance	23
8. Conclusions	27
9. References	28
Appendix 1. Methods of chemical analysis of water samples	30
Appendix 2. Chemical analyses	33
Appendix 3. Intercalibration	35

SUMMARY

There is a considerable interest in determining the effects of acidic deposition on various environments, e.g. surface waters. One of the important issues is to evaluate and to set limits on the deposition of acidic compounds according to the effects on the ecosystem. The limit, or critical loads of acidity to an environment, is defined as "The highest deposition of acidifying compounds that will not cause changes leading to long-term harmful effects on ecosystem structure and function."

Critical load of acidity to surface waters and exceedance of critical load were estimated, using standard methods modified for northern Moravia and Silesia, the north eastern part of The Czech Republic.

Water samples were mainly taken from small forest streams. Few natural lakes exist in this region, and most of the landscape is influenced by agricultural activities. The small forest streams were the only available surface waters with little or no pollution from local sources.

High critical loads to surface waters were calculated for the examined region. This high critical load reflects the geological composition of the area and its weathering rate. The average value of critical load from this Czech region was approximately twenty times higher than the corresponding value for southern Norway.

Critical loads for soils were lower than critical loads for surface waters in parts of the examined region.

Although the deposition of acidifying components in this area was high (5 gS/m²/year compared to 1-2 g in South Norway), no part of the examined region showed exceedance of critical load for surface waters.

The calculated values of exceedances show high negative figures for most of the region, indicating that there exists a reserve for additional acid deposition. An increase of 50 % of acid deposition would cause exceedance of only 13 % of the studied area.

Scattered water analyses from several other parts of The Czech Republic indicate both low critical loads and exceedance of critical load in various regions (e.g. Bohemia). The studies of critical loads will therefore continue, and in 1994 northern Bohemia will be surveyed.

1. INTRODUCTION

There has been a considerable scientific and political interest in determining the effects of acidic deposition on various environments. Beyond the linkage of atmospheric deposition of strong acids to effects on forests, lakes, crops, human health and materials, one of the important issues is to evaluate and set limits on the deposition of acidic compounds. The limit, or critical load of acidity to an environment, is defined as "the highest deposition of acidifying compounds that will not cause changes leading to long term harmful effects on ecosystem structure and function" (Nilsson and Grennfelt, 1989).

Criteria for "unacceptable change" are set relative to effects on terrestrial and aquatic organisms. Both sulphur and nitrogen contribute to the total input of acidic compounds to an ecosystem. The purpose of determining critical loads is to set goals for future deposition rates of acidifying compounds such that the environment is protected. Critical loads are determined separately for different receptors, such as soils and surface waters. The critical load for a particular receptor will vary from site to site, depending on its inherent sensitivity. At a given site the critical load for soils may differ from the critical load for surface water. In order to protect the whole environment the ultimate critical load should not exceed the lowest of these critical loads.

Critical loads for the acidification of surface waters have been most thoroughly studied with respect to sulphur. Critical loads of sulphur were exceeded long ago in large regions in many countries, and the effects are manifested e.g. in the form of acidic fishless lakes in Scandinavian countries.

Under the auspices of the Convention on Long-Range Transboundary Air Pollution (the "Geneva Convention"), a "Task Force for Mapping the Critical Loads and the Areas where the Critical Loads are Exceeded" has been formed. A Manual for calculating critical loads and their exceedances both for forest soils and for surface waters has been worked out (Sverdrup et al. 1990). Critical loads of acidity and the exceedance for sulphur and nitrogen to surface waters was first mapped for Norway, and a project under the Nordic Council of Ministers has mapped critical loads and their exceedance for surface waters for the three Nordic countries Finland, Norway and Sweden (Henriksen et al. 1990).

2. DEFINITIONS

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

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

* Biological indicator: Selected organism(s) or populations which are sensitive to chemical changes as a result of atmospheric inputs of sulphur and nitrogen (forest, fish, invertebrates).

* Critical chemical value: The value of a critical chemical component or combinations of components above or below no harmful response in a biological indicator occurs (pH, ANC, Al/Ca ratio).

The critical load definition provides a framework for making numerical estimates of the load at which adverse effects occur. Such estimates may be based upon a number of different methods, and the selection of a method depends to a large extent upon the receptor chosen and the availability of relevant data for the calculations. The effects on sensitive biological indicators are used to identify harm to freshwater systems. Organisms are often efficient integrators of the chemical conditions in their environment and may thus provide a convenient means of measuring effects. The methods for calculating critical loads of acidity to freshwaters use chemical data. The critical chemical value is based on knowledge of the ecological tolerance of sensitive biological species to changes in water chemistry. Resistivity of the whole ecosystem, landscape, territory is determined by a complex of natural factors, in particular by geochemical weathering processes, and it is expressed as a critical load value.

3. CALCULATING CRITICAL LOADS OF ACIDITY TO FRESHWATER

The Task Force on Mapping has compiled a manual for calculating critical loads and their exceedances. It describes three different methods for calculating critical loads for surface water, ground water and soil:

1. The Steady-State Water Chemistry Method
2. The Steady-State Mass Balance Method
3. Dynamic Modelling Methods

The first method is only applicable to surface waters, while methods 2 and 3 can be used for soil, ground water and surface water. The first two methods are static, i.e. they compute the critical load assuming steady-state with respect to the inputs from the atmosphere. The dynamic modelling methods also take into account time-dependent processes. The Steady-State Water Chemistry method has been applied on a wide scale to the Scandinavian lakes. The method was developed at NIVA (Henriksen et al. 1990) and has been accepted internationally as a standard technique. In a newer version of this model (Kämäri et al. 1992), acidity caused by both sulphur and nitrogen is included.

The steady-state water chemistry method

Acid Neutralization Capacity (ANC) is used as the chemical criterion for sensitive indicator organisms in surface waters. ANC is defined as the difference between non-marine base cations (BC)* and strong acid anions (AN)*. Non-marine contributions are indicated by an asterisk *, and brackets [] denote concentrations:

$$[\text{ANC}] = [\text{BC}]^* - [\text{AN}]^* \quad (1)$$

The critical load for surface water is related to the original leaching of base cations from the catchment area. The critical load, CL, of acidity for a given indicator organism is given by:

$$\text{CL} = ([\text{BC}]_0^* - [\text{ANC}_{\text{limit}}])Q - \text{BC}_{\text{dep}}^* \quad (2)$$

where BC_0^* is the pre industrial non-marine base cation concentration, $\text{ANC}_{\text{limit}}$ is the critical ANC-concentration for the organism considered, Q is the mean annual runoff and BC_{dep}^* is the non-marine base cation deposition. To compute the critical load, values for BC_0^* have to be estimated from present-day water chemistry data (Henriksen et al. 1990) according to the formula:

$$[\text{BC}]_0^* = [\text{BC}]_t^* - F \cdot ([\text{SO}_4^{2-}]_t^* - [\text{SO}_4^{2-}]_0^*) \quad (3)$$

Here, $[\text{BC}]_t^*$ and $[\text{SO}_4^{2-}]_t^*$ are present day concentrations of non-marine base cations and sulphate, respectively, $[\text{SO}_4^{2-}]_0^*$ is the pre-industrial concentration of non-marine sulphate and F is a factor that compensates for the base cation leaching due to acidification (Brakke et al. 1990):

$$F = \sin [\text{BC}]_t / S \quad (4)$$

Here, S is a factor that has to be estimated from empirical data for the area under consideration. For the Scandinavian countries S is set to 400. No empirical data exists for the water quality of the Czech study area. To simplify the calculations, the sinus function was omitted and the F-factor was defined as $[\text{BC}]_t / 1000$ to cover the base cation range of the Czech streams. If the value $[\text{BC}]_t$ was higher than 1000, it was set to 1000 to give F the value of 1.

$[\text{SO}_4^{2-}]_0^*$ is defined as the original background concentration of non-marine sulphate. It consists of both an atmospheric background input and a catchment derived input. For the low acid deposition areas of Norway, $[\text{SO}_4^{2-}]_0^*$ was calculated to be $15 + 0.16 [\text{BC}]^*$ from empirical data (Henriksen et al. 1990). No such data were available from The Czech Republic. However, due to the geographical location in central east Europe and more geological sulphur in the region, the $[\text{SO}_4^{2-}]_0^*$ was set to 50 ueq/l.

The sum of base cation concentrations including correction for sea salt was calculated from:

$$[\text{BC}]_t^* = [\text{Ca}^{2+}]^* + [\text{Mg}^{2+}]^* + [\text{Na}^+]^* + [\text{K}^+]^* \quad (5)$$

Thus, the pre-industrial non-marine base cation concentration for northern Moravia and Silesia was calculated by the simplified formula:

$$[\text{BC}]_0^* = [\text{BC}]_t^* - [\text{BC}]_t^* / 1000 \cdot ([\text{SO}_4^{2-}]_t^* - [\text{SO}_4^{2-}]_0^*) \quad (6)$$

The present exceedance of the critical load of acidity (CL_{ex}) is calculated by comparing the critical load from equation (2) with the present non-marine sulphate deposition, $SO_4^*_{dep}$ and the present leaching of nitrate from the catchment:

$$CL_{ex} = SO_4^*_{dep} + NO_3le - CL \quad (7)$$

Fish was selected as a biological indicator for a critical value of ANC (Lien et al. 1992). A study of 1000 Norwegian lakes (Henriksen et al. 1988, 1989) evaluated an extensive material on fish status and water chemistry. These data were used for calculation of probability of damage of fish populations at the different levels of ANC. Based on these results, a critical value $ANC_{limit} = 20$ ueq/l was considered appropriate for calculation of critical loads (Lien et al. 1992). This value was also used for to Czech surface waters.

The value of 20 ueq/l is assumed to represent the annual average value of the water chemistry of the locality. Selection of this same value for Czech surface waters is suitable also from the point of view of comparison of results from other regions.

4. DESCRIPTION OF THE SAMPLING AREA: NORTHERN MORAVIA AND SILESIA

4.1 Location of the study area

The sampling and analyses of surface waters were performed in 1993 in the area of northern Moravia and Czech Silesia. Geographical limits of the study area are formed by Kralicky Sneznik Mts. in the west, the boundary between The Czech Republic and Slovakia in the east and south - east, the boundary with Poland in the north and a line Hanusovice - Rymarov - Moravsky Beroun - Odry - Valasske Mezirici - Roznov pod Radhostem-Horni Becva in the south and south-west (Fig. 1 and 2).

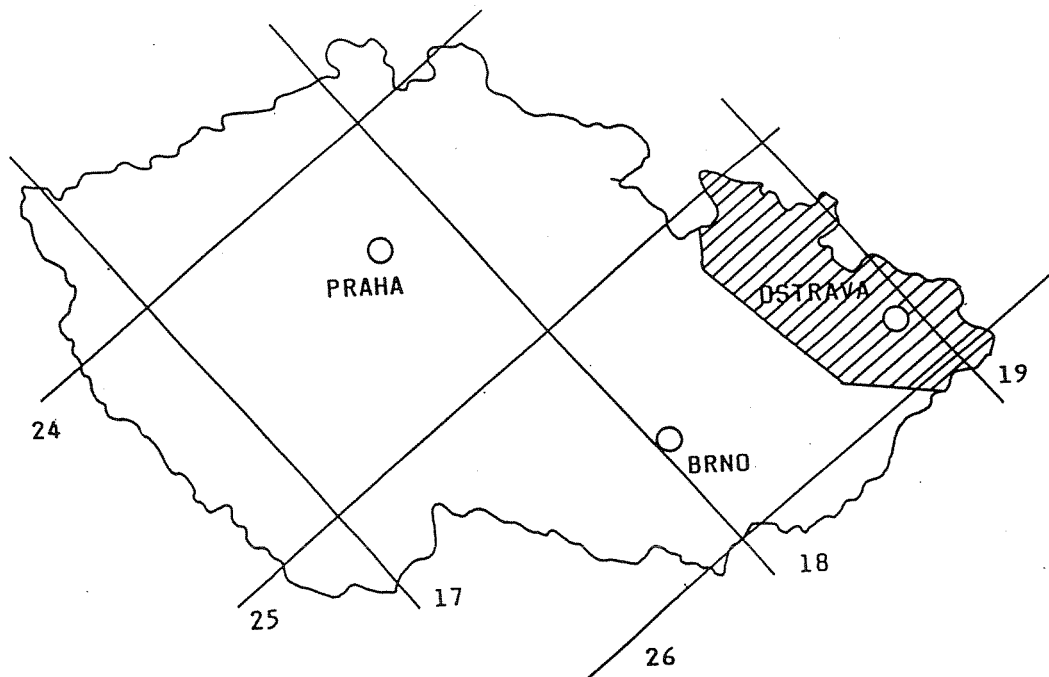
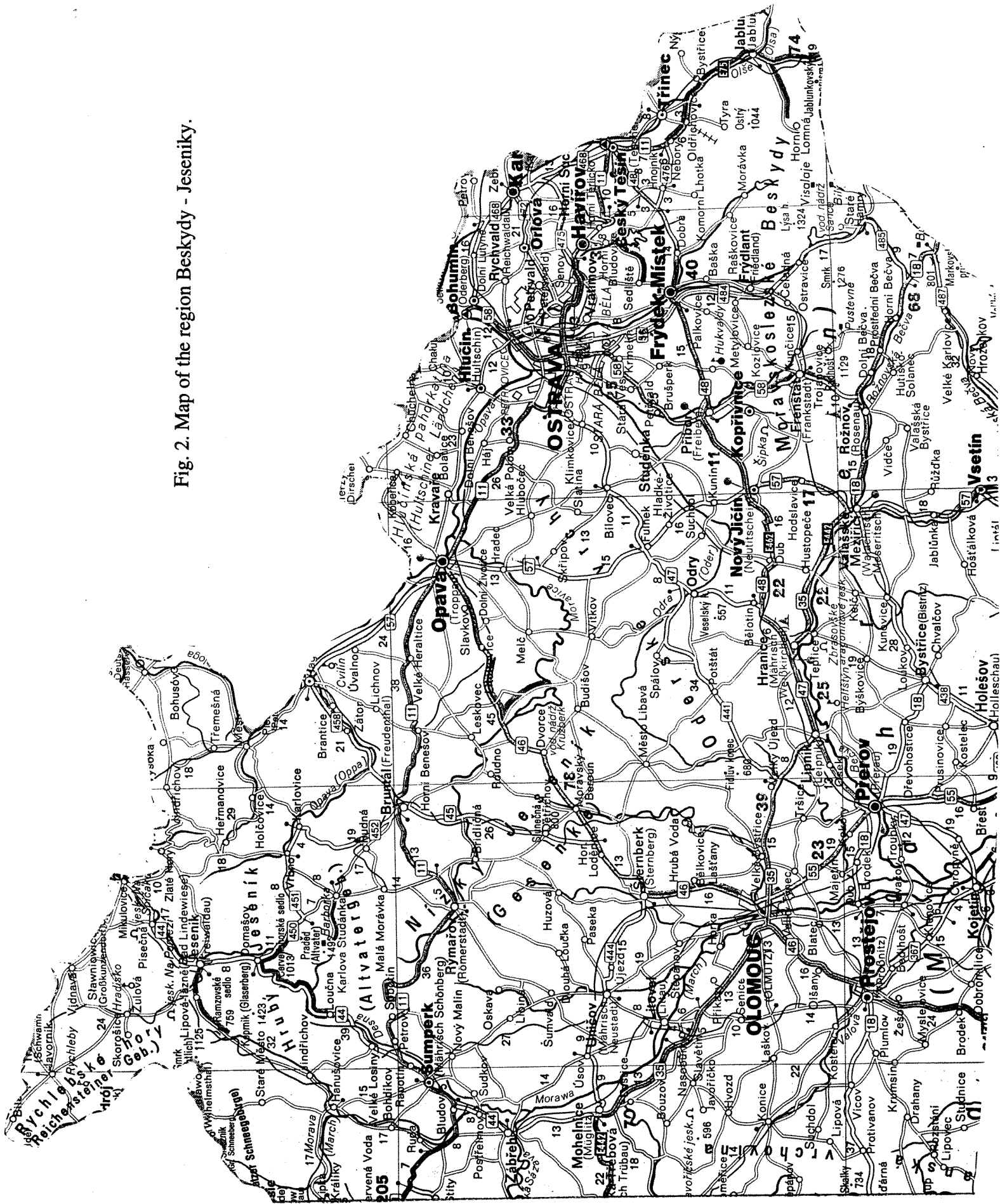


Fig.1 The studied area of The Czech Republic including the EMEP grids (The Co-operative Program for the Monitoring and Evaluation of the Long-Range Transmission Air Pollutants in Europe).

Fig. 2. Map of the region Beskydy - Jeseníky.



This sampling area includes the following geographical units (from east to west): Kralicky Sneznik Mts. (with the highest summit 1423 m a.s.l.), Rychlebske hory Mts. (highest point Smrk, 1125 m a.s.l.), Vidnava Upland between Rychlebske hory Mts. and Hruby Jesenik Mts., and further to the west, Hruby Jesenik Mts. (highest summit Praded 1491 m a.s.l.). Nizky Jesenik Mts. (Low Jesenik) at lower altitude (Slunecna, 800 m a.s.l.) follow in the south-east, with Oderske vrchy (Odra Hills) in the southern part. Nizky Jesenik Mts. border to the south-east depression of the Moravian Gate, and north-east to the Opava Upland. The Moravian Gate passes in the north-east direction into Ostrava Basin. South-east of the Moravian Gate and Ostrava Basin, the eastern part of the studied area is formed by Podbeskydska pahorkatina Hills and by Moravskoslezske Beskydy Mts. The small part of the study area, east of Moravskoslezske Beskydy Mts. belongs to Slezske Beskydy Mts.

The largest part of the territory belongs to the catchment of River Odra, which originates in the Odra Hills and flows through the Moravian Gate into Poland and the Baltic Sea. The main tributaries of Odra are the River Ostravice (with tributaries Moravka and Lucina) draining water from northern part of Moravskoslezske Beskydy Mts., and River Olse (with tributaries Hluchova, Lomna, Kopytna, Tyrka, Ropicanka, Reka and Stonavka). Smaller tributaries of the River Odra are Jicinka, Sedlnice, Lubina and Ondrejnice. All of them have sources in Podbeskydska pahorkatina Upland and they join the River Odra in the Moravian Gate.

The main tributary of the River Odra is Opava with sources in the Hruby Jesenik Mts. where it originates by confluence of Bila Opava (White Opava), Stredni Opava (Middle Opava) and Cerna Opava (Black Opava). Catchment of River Moravice, a tributary of Opava, corresponds to the big part of Nizky Jesenik Mts. River Opavice, an other tributary of Opava, flows from the western part of Nizky Jesenik Mts. River Osoblaha with a smaller catchment flows in northern direction into Poland. River Bela from the northern side of Hruby Jesenik Mts., River Vidnavka, and small water streams from Rychlebske hory Mts. on the Polish territory join River Kladska Nisa, and form tributaries to the River Odra.

The smaller part of the studied area is part of the catchment of River Morava, one of the largest tributaries of Danube which flows into the Black Sea. River Morava has sources in the vicinity of Kralicky Sneznik and flows southwards at the western boundary of the studied territory. River Morava has the tributaries Branna and Desna coming from Hruby Jesenik Mts. Southern part of Moravskoslezske Beskydy Mts. is drained by the River Becva, an other tributary of the River Morava.

4.2 Geological composition of the area

The bedrock geology of the studied area is illustrated by geological map (scale 1:1 000 000) in Fig. 3.

The main geological formations in the studied area are:

- 1.** Crystalline rocks of Hruby Jeseník Mts. (Silesikum) and Orlické hory Mts.-Klodskeo (Lugikum).
- 2.** Paleozoic rocks (Devonian and Lower Carboniferous) of Nizky Jeseník Mts.
- 3.** Cretaceous and Paleogene rocks of Moravskoslezské Beskydy Mts. and Podbeskydská pahorkatina Hills.
- 4.** Neogene and Quaternary rocks of Moravian Gate and Ostrava Basin with Opava Uplands.

4.3 Climatological conditions

Data on precipitation and evaporation which are used for estimation of runoff, are most important for determination of critical loads. A map of annual mean precipitation for the period between 1981 and 1990 (Czech Hydrometeorological Institute, Branch Ostrava) is presented in Fig. 4, and a map of annual mean total evaporation from free water surface for the same period is in Fig. 5.

Annual mean precipitation reaches values above 1400 mm in Hruby Jeseník Mts., and above 1500 mm in Moravskoslezské Beskydy Mts., the highest precipitation in The Czech Republic. Precipitation increases from the piedmont area to the top of the mountain ridges of Beskydy Mts. Frydek-Místek (290 m a.s.l.), approximately 16 km from the foot of Moravskoslezské Beskydy Mts., has 910 mm annual mean precipitation, Ostravice (417 m a.s.l.) in a distance approximately 2 km has 1130 mm. In this mountain area precipitation increases with altitude above sea level.

Northern Moravia has a continental seasonal distribution of precipitation, with high precipitation during summer (June - July), and minimum in winter. Average percentage of precipitation for Moravia are; spring - 23 %, summer - 37 %, autumn - 23 %, and winter - 17 %. Summer precipitation maximum is more pronounced in the lowlands than in the mountains. In northeastern Moravia, the precipitation maximum is often shifted to the end of summer (August).

Evaporation maps (Czech Hydrometeorological Institute) are for free water surface. Therefore, it was not possible to determine the runoff by just subtracting evaporation from precipitation. The calculation of runoff was done by reducing the precipitation value by 30 % for evaporation for all grids.

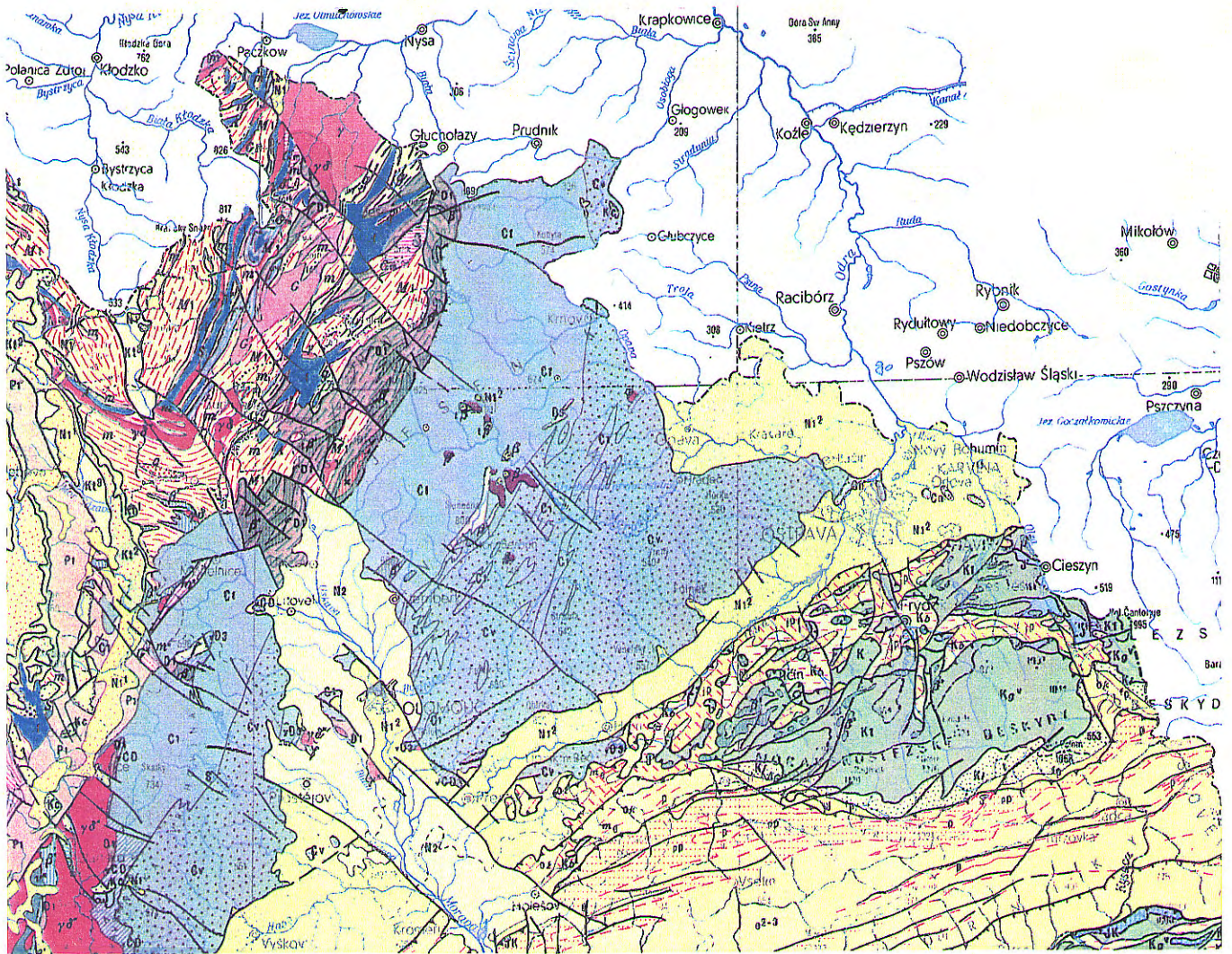
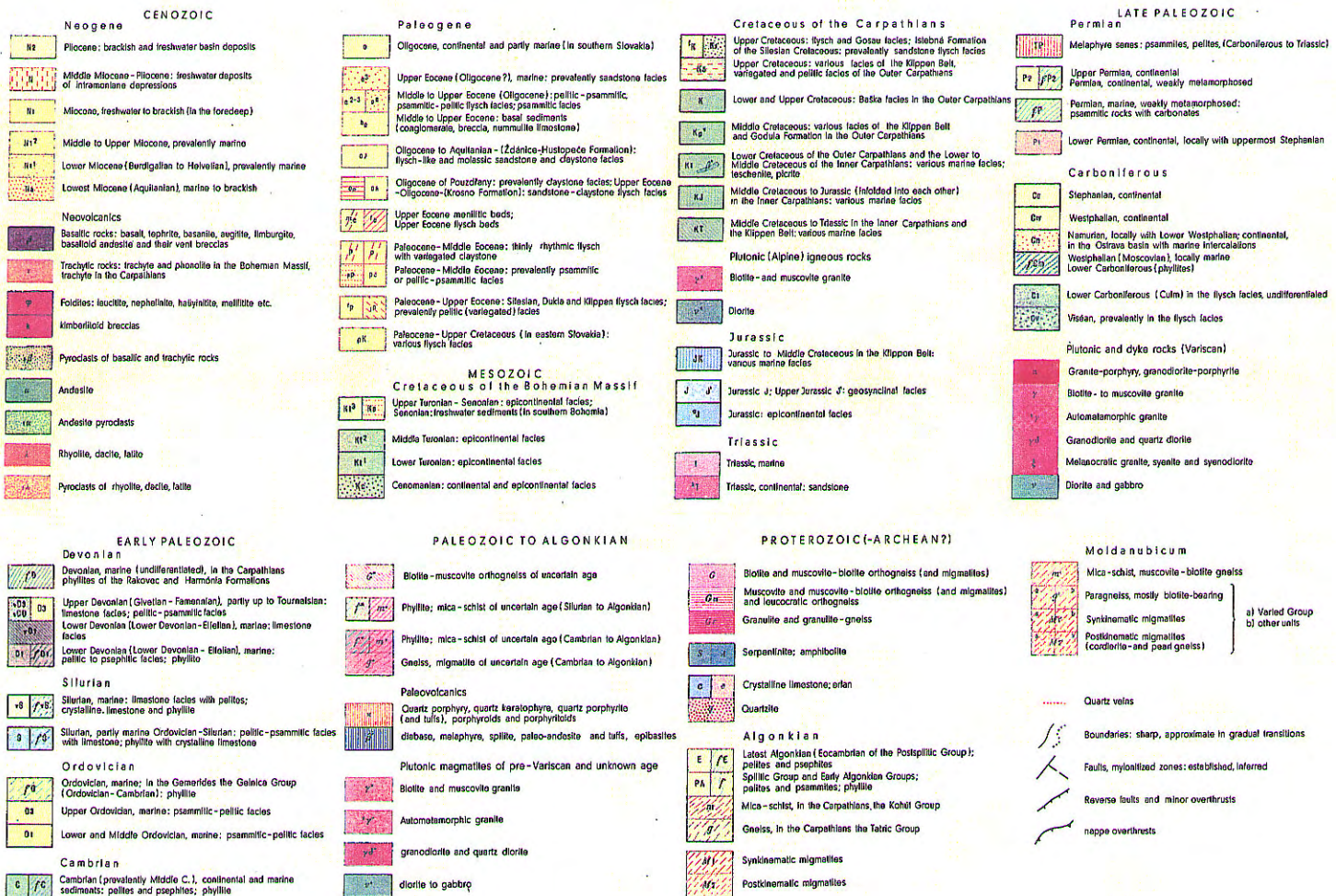


Fig. 3. Geological map of northern Moravia and Silesia.



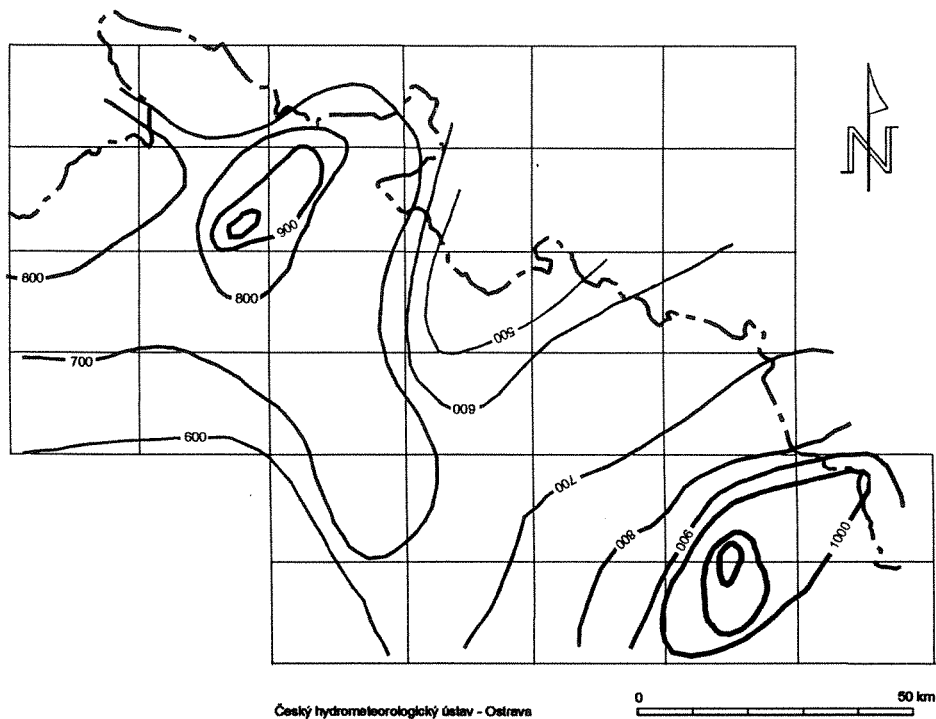


Fig. 4. Annual average precipitation in mm for the period 1981 - 1990.

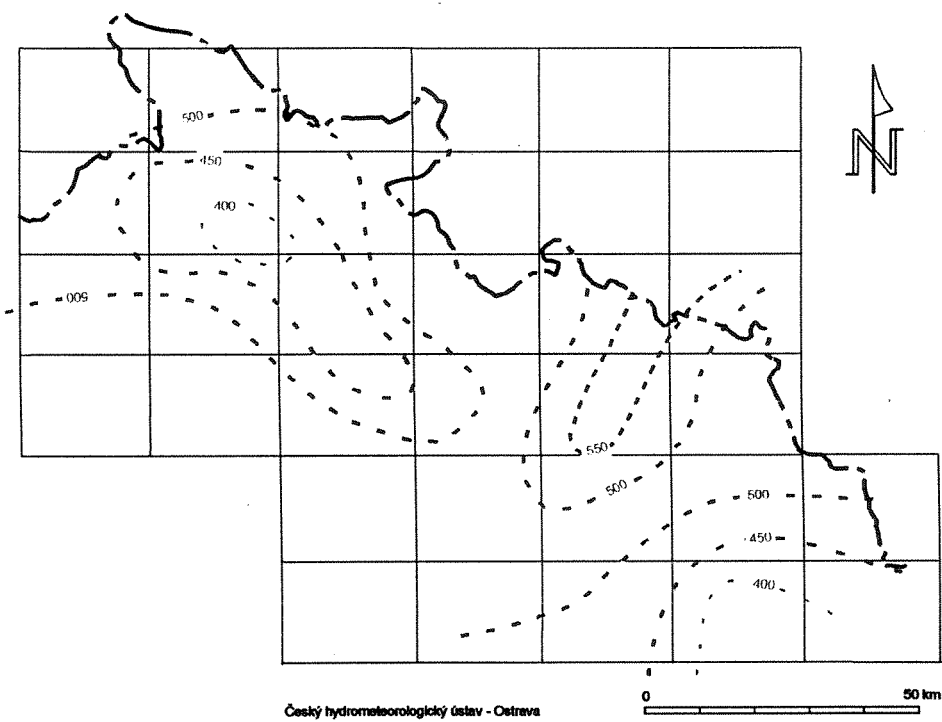


Fig. 5. Annual average evaporation in mm from free water surface for the period 1981 - 1990.

4.4 Soil

The prevailing soil types of the area of Hruby Jeseník Mts., Rychlebské hory Mts. and Kralický Sněžník are soils of the cambisol group. At lower altitude the soils are modal, and to a lesser extent acid or podzol cambisols. At higher altitude there are acid cambisols and humic podzols. In climatically-exposed conditions, especially at highest altitude, rankers and poorly developed cambisols occur. Some areas are also covered by gleyic cambisols, and at the highest altitudes peat bogs occur.

Nizky Jeseník Mts. have relatively monotonous structure of soil cover. Modal cambisols prevail over approximately two thirds of the whole territory. Gleyic cambisols have small extent and podzol cambisols even less extent. Rankers have negligible extent. Quaternary loess frequently covers the modal cambisols.

The Moravian Gate area of Ostrava Basin have low-land types of soils of flat land on Quaternary sediments. Loess occurs frequently as soil substratum. The majority of the area belongs to the group of fluvisols (modal and acid fluvisol), luvisols (modal and gleyic types) and gleysols (modal, acid and humic gley). These types of soils are widespread also in Opava lowland along river Opava and in the environs of Osoblaha.

Cambisols (modal cambisols) together with their transitions to stagnosols are dominant in Podbeskydská pahorkatina Upland. Stagnosols occur usually on loess substratum. More than 80% of territory of Moravskoslezské Beskydy is covered by soils of cambisol group - modal to acid cambisols. The remainder is humic podzols. Lesser areas are covered by stagnosols (transition to cambisols) and gleysols. Rankers occur on slopes in higher altitudes.

Typical vertical zonation of soils is developed in the mountainous regions of Hruby Jeseník Mts. and Moravskoslezské Beskydy Mts.

4.5 Vegetation

Forest is the prevailing vegetation in the mountain regions of Hruby Jeseník and Moravskoslezské Beskydy. In the region of Nizky Jeseník Mts. forests are approximately in balance with areas of fields, but in some areas the forests have lesser extent. The region of the Moravian Gate and Ostrava Basin is almost prevalently used for agriculture.

Norway spruce (*Picea abies*) dominates the forests of Hruby Jeseník Mts., mostly as monocultures, to a lesser extent in mixed forests. The most frequent admixture in spruce forest is beech (*Fagus sylvatica*) which also forms small islands of original beech forest. The higher boundary of spruce forest in Hruby Jeseník Mts. is 1200 m a.s.l. where natural spruce forests pass into mountain meadows and park-type forest formed by dwarf forms of spruce in mixture with mountain ash (*Sorbus aucuparia*).

Spruce forest dominates also in the Nizky Jeseník Mts. The most important admixture in spruce forest is beech. European silver fir (*Abies alba*) also occurs in older forests. At lower altitudes the typical forests are oak (*Quercus robur*) and Scots pine (*Pinus sylvestris*).

In the region of Moravian Gate, Ostrava Basin, Opava Upland and most of area of Podbeskydská pahorkatina Upland, the forest acreage is very low. Coniferous forests which cover approximately two thirds of the total forest area, are mostly spruce, and only

small part is pine. Oak is the most common broad-leaved tree (approximately 10%); less frequent are lime (*Tilia cordata*), alder (*Alnus glutinosa*), birch (*Betula pendula*), beech, ash (*Fraxinus excelsior*), and maple (*Acer pseudoplatanus*). Forests usually cover small areas, mostly under 100 hectares.

In Moravskoslezské Beskydy Mts. the prevailing coniferous forests cover approximately 70% of the area, and they are formed almost entirely by spruce. Other coniferous trees like European silver fir, Scots pine and larch (*Larix decidua*) have negligible representation. There are prevailing pure spruce forest or spruce forests with very small admixtures, most often formed by beech. Beech forms about 90% of deciduous forests; only small admixtures are formed by other broad-leaved trees - maple and birch. Spruce forests also cover mountain ranges of Beskydy Mts. with exception of the highest summits. Beech reaches altitudes of 1100 m a.s.l.

5. MATERIAL AND METHODS

5.1 Seasonal variations of element concentrations in surface waters

The method of steady state chemistry assumes that values of ion concentrations used for calculations correspond to the annual mean values. It is therefore important to compare long-term measurements with values from the potential period of sampling. Seasonal and annual variations of water parameters are illustrated from the brook Recice. This is one of the tributaries of the Reservoir Sance in Moravskoslezské Beskydy Mts. Fig. 6 shows the concentrations of Ca, Mg, Na, K, Cl, SO₄, NO₃ (mg/l), alkalinity (mmol/l), pH and electrical conductivity (mS/m) for the period from April 1989 to November 1993. The monitoring is performed by Management of River Odra Catchment (Povodi Odry) in Ostrava which provided these analyses.

The results show pronounced variations and larger deviations from long-term averages during spring months. Second half of year is relatively stable, and is therefore more suitable for sampling of surface waters for critical loads assessment. Comparison of annual averages with values of parameters for October confirmed that this month is a suitable period for sampling.

5.2 Sampling

Sampling was performed between 6th and 27th October 1993. Only small rivers and streams with their entire catchments in forest areas were chosen. This was done in order to avoid local contamination by industry, agriculture and housing. In regions with sufficient numbers of suitable water streams (Moravskoslezské Beskydy Mts. and Jeseník Mts.) two samples were taken per grid (113 km²). In some areas it was impossible to locate forest rivers. The lowest acceptable sampling density was one sample per 100 km². In the area of Moravian Gate, Ostrava Basin, Opava Upland and also in large part of Nizky Jeseník Mts. it was necessary to sample every suitable stream. Because of lack of suitable streams in the highly contaminated region of Ostrava Basin, several samples were taken from springs. The sampling localities are shown in Fig. 7.

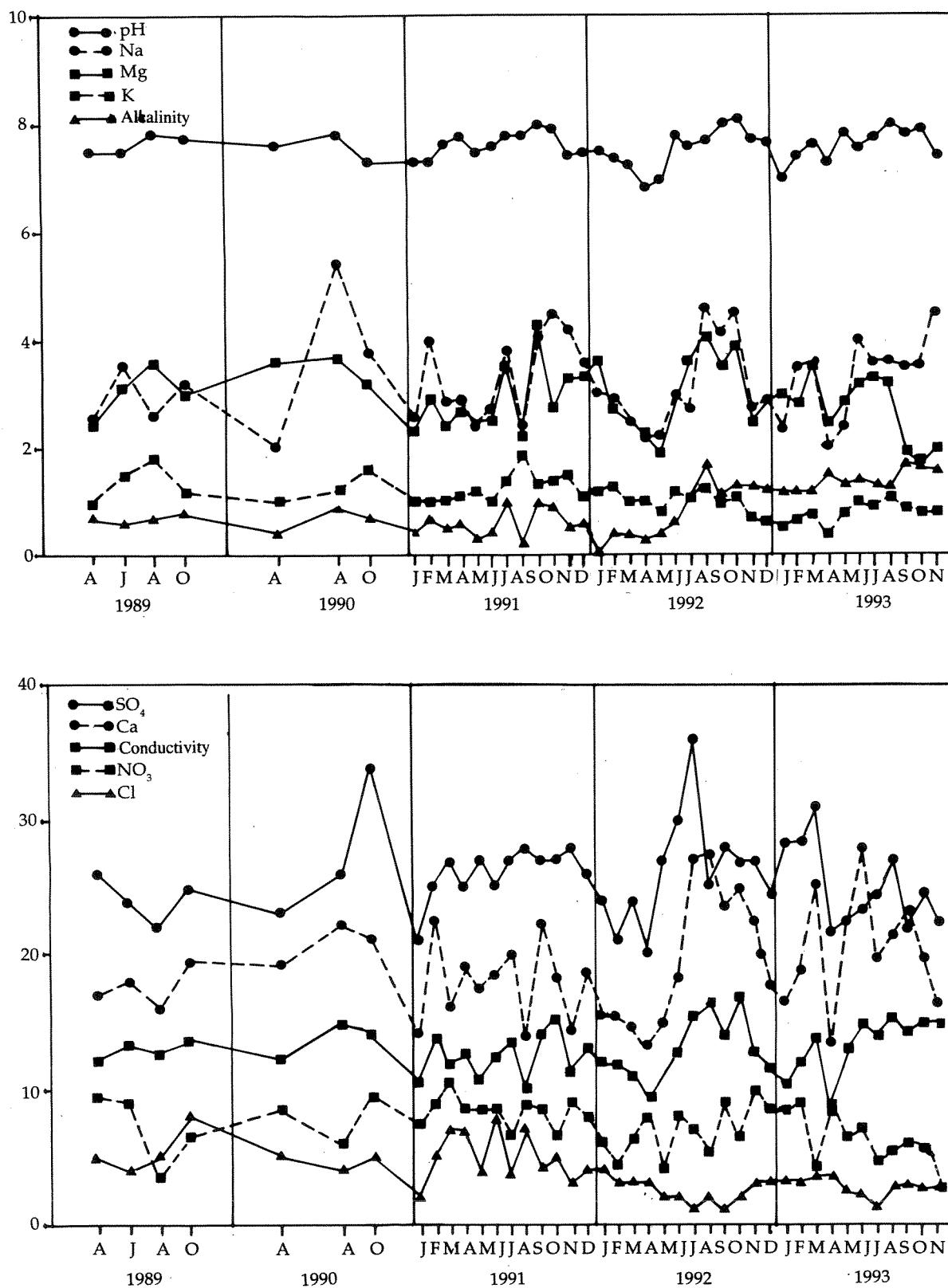


Fig. 6. Values of pH, alkalinity and concentrations of magnesium, sodium and potassium (upper), and calcium, sulphate, chloride, nitrate and conductivity (lower) for the River Recce from April 1989 to November 1993.

To enable comparison with critical load analysis for lakes, samples were also taken from flooded granite quarries and one lake Velke mechove jezirko at Rejviz. Two more samples were taken from flooded quarries in the area of Zulova Granitoid Massif .

The 109 water samples from the small streams and springs were taken from geological substratum as follow:

1. Crystalline rocks of Hruby Jesenik Mts. and Kralicky Sneznik Mts: 36 samples.
2. Devonian and Lower Carboniferous of Nizky Jesenik Mts: 21 samples.
3. Cretaceous and Paleogene of Moravskoslezske Beskydy Mts. and Podbeskydska pahorkatina Upland: 44 samples.
4. Neogene and Quaternary: 8 samples (5 in the area of Ostrava Basin, 1 in Moravian Gate and 2 samples in Opavska pahorkatina Upland)

In addition, six samples taken in 1992 and analysed at NIVA were included.

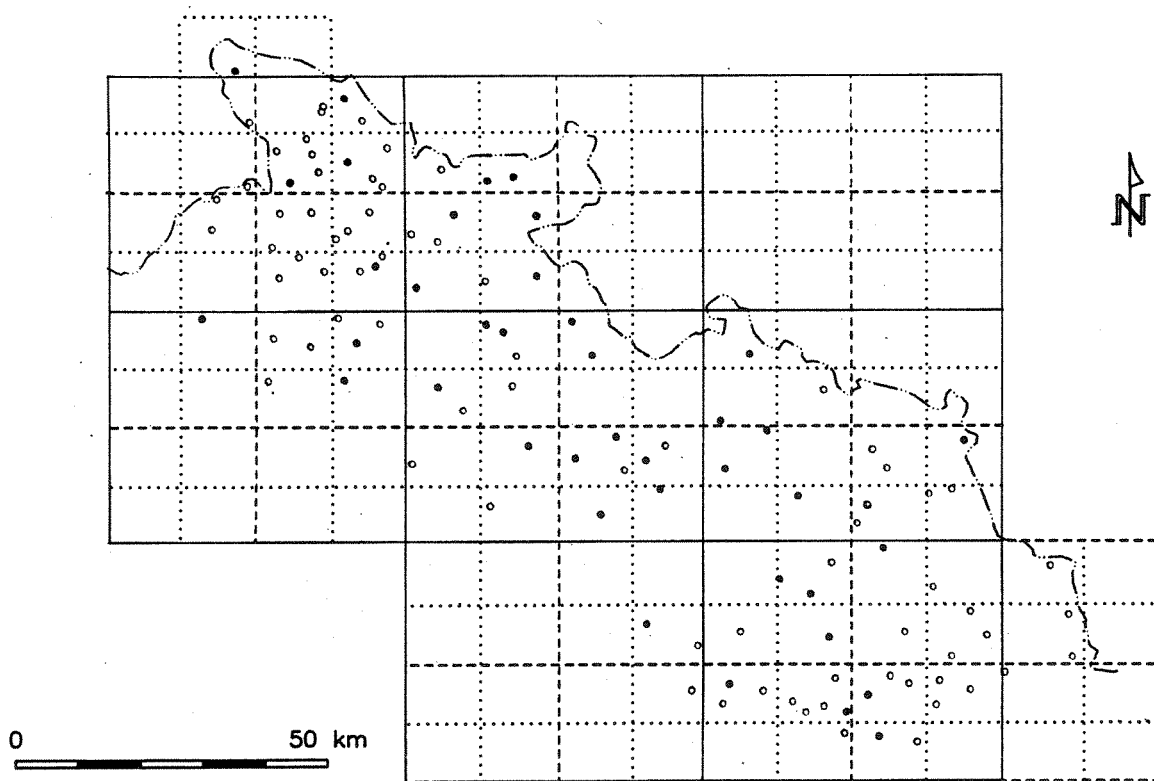


Fig. 7 Sampling sites in northern Moravia and Silesia. Solid circles are sites used for calculations of critical loads.

5.3 Chemical analyses

The methods used for conservation and analysis of water samples are given in Appendix 1. The results of the chemical analyses are presented in Appendix 2. The table includes pH values, specific conductivity, turbidity, particulate matter (non-dissolved), total dissolved matter, total organic carbon (TOC) and values for calcium, magnesium, sodium, reactive aluminium (Al_r), non-labile aluminium (Al_{nl}), ammonium, chloride, sulphate, nitrate and alkalinity.

Table 1 shows the difference between cations and anions for the various water samples. For a number of samples there was a considerable difference between sums of cations and anions. A maximum of 30 % difference was accepted.

In order to identify systematic reasons for the differences, 12 water samples from the Czech laboratory were also analysed at NIVA. The parallel analyses are presented in Appendix 3. Excellent correlation was seen for calcium, and quite good agreements occurred for sodium, sulphate, and with a few exceptions also for nitrate. Chloride was systematically higher in the Czech analysis while magnesium showed both higher and lower values. The ionic balance for these 12 samples were recalculated using the six parameters analysed at NIVA together with the other parameters from the Czech laboratory. With exception of one sample, the ionic balance improved, and with exceptions of two samples, the balance reached an acceptable limit of 30 % deviation.

The analyses of chloride and magnesium and may be also alkalinity should be adjusted in the Czech laboratory prior to further analyses of parameters for critical load calculations. For 1994, a double set of water samples will be taken from each sampling locality for possible re-analysis, possibly at the NIVA laboratory.

6. CRITICAL LOADS OF NORTHERN MORAVIA AND SILESIA

Values of critical loads of acidity CL and values of their exceedances CL_{ex} were calculated according formula described in Chapter 3. ANC_{limit} was set to 20 ueq/l. Runoff was calculated from annual average of precipitation minus 30 % reduction for evaporation. Deposition value of base cations was used according to the International Institute for Applied System Analysis (IIASA), following recommendations of International Co-ordination Centre for Effects (Hetteling et al. 1991). EMEP grid No. 25-18 which accommodates all studied area has value of base cation deposition according IIASA: $BC_{dep} = 42 \text{ keq/km}^2/\text{year}$. The EMEP grids is presented in Fig. 1.

Sulphur deposition value for EMEP grid No.25-18 was used according Czech Hydrometeorological Institute, Prague, after recalculation: $S_{dep} = 254 \text{ keq/km}^2/\text{year}$.

Both values for deposition of base cations and sulphur are comparable with data for the depositions at the observation stations of Czech Hydrometeorological Institute at Bily Kriz, Moravskoslezske Beskydy Mts. and stations of Research Water Institute (Ostrava Branch) at Moravka and Vratimov. Because validity of data from these stations is restricted to their particular localities, values for international EMEP grid were preferred. However, relatively high variability of SO_2 concentrations in the atmosphere are shown in the map (Fig. 8). Therefore, data of specific deposition in the study area can be useful for later calculations of critical loads and exceedances.

Table 1. Sum of cations, anions, and their differences both in equivalence value and percentage for each sampling locality. Data sets used for calculation of critical load are marked.

Sample	Σ_k	Σ_{an}	δ	δ	Sample	Σ_k	Σ_{an}	δ	δ
	$\mu\text{eq/l}$					$\mu\text{eq/l}$			
				%					%
1	2856.58	3856.82	-1000.24	-35.01	60	2416.68	850.93	1565.75	64.78
2	1468.74	2677.89	-1209.15	-82.32	61	2211.10	1010.47	1200.63	54.30
3	1108.82	2103.70	-994.88	-89.72	▶62	2652.21	1969.61	682.60	25.73
4	2563.51	3727.55	-1164.04	-45.40	63	2636.23	1233.41	1402.82	53.21
5	1088.51	1769.17	-680.66	-62.53	64	1582.32	625.74	956.58	60.45
6	948.49	1613.06	-664.57	-70.06	65	1550.42	764.43	785.99	50.69
7	672.95	1425.88	-752.93	-111.88	▶66	2310.42	1707.15	603.27	26.11
8	1019.37	1740.35	-720.98	-70.72	67	1680.76	732.55	948.21	56.41
9	1065.93	1731.73	-665.80	-62.46	68	1578.87	832.93	745.94	47.24
10	1615.10	2283.08	-667.98	-41.35	▶69	1537.28	1188.62	348.66	22.68
11	911.29	1199.16	-287.87	-31.58	70	2841.78	1317.83	1523.95	53.62
12	1193.78	2163.80	-970.02	-81.25	71	2188.05	969.91	1218.14	55.67
13	1067.94	1640.87	-572.93	-53.64	72	2075.06	1007.14	1067.92	51.46
14	1155.09	1225.70	-70.61	-6.11	73	2609.66	1561.03	1048.63	40.18
▶15	1018.31	1201.08	-182.77	-17.94	74	2951.43	1521.30	1430.13	48.45
▶16	1002.37	1125.02	-122.65	-12.23	▶75	4317.40	4084.99	232.41	5.38
▶17	889.79	1065.55	-175.76	-19.75	▶76	3898.35	2600.03	1298.32	33.30
18	806.73	1185.57	-378.84	-46.95	▶77	4597.07	3368.01	1229.06	26.73
▶19	4974.35	5380.73	-406.38	-8.16	▶78	3809.78	3249.82	559.96	14.69
▶20	893.07	1033.85	-140.78	-15.76	▶79	3903.02	3426.80	476.22	12.20
21	4833.21	7434.70	-2601.49	-53.82	80	2715.21	1555.22	1159.99	42.72
▶22	6550.38	5627.31	923.07	14.09	81	2371.10	1145.51	1225.59	51.68
23	1782.01	2360.45	-578.44	-32.45	82	2320.39	1248.57	1071.82	46.19
24	1262.59	1977.56	-714.97	-56.62	▶83	2497.41	2011.79	485.62	19.44
25	1108.08	1642.18	-534.10	-48.20	84	3828.12	1810.14	2017.98	52.71
26	948.53	1473.61	-525.08	-55.35	85	3466.73	2377.09	1089.64	31.43
27	1195.41	1680.63	-485.22	-40.59	▶87	3425.07	2940.74	484.33	14.14
28	2197.64	2882.59	-684.95	-31.16	▶88	2981.06	3399.94	-418.88	-14.05
29	5994.79	8163.24	-2168.45	-36.17	▶89	1944.96	1645.93	299.03	15.37
▶30	2937.01	3668.67	-731.66	-24.91	▶90	2184.14	1911.75	272.39	12.47
31	1227.91	1726.61	-498.70	-40.61	91	2022.07	1340.61	681.46	33.70
32	5659.54	9131.94	-3472.40	-61.35	92	1951.76	1206.93	744.83	38.16
33	14821.90	18299.88	-3477.98	-23.47	▶93	1826.68	1690.47	136.21	7.45
34	1320.37	1817.88	-497.51	-37.67	94	1381.77	765.97	615.80	44.56
▶35	4519.00	5845.24	-1326.24	-29.34	▶95	5258.15	4171.32	1086.83	20.66
36	1270.33	2282.74	-1012.41	-79.69	96	2440.27	1383.22	1057.05	43.31
37	1511.61	2664.02	-1152.41	-76.23	97	1447.29	876.75	570.54	39.42
38	2011.60	2947.49	-935.89	-46.52	98	1361.65	778.62	583.03	42.81
39	4951.69	5580.36	-628.67	-12.69	99	879.94	531.67	348.27	39.57
▶40	3906.35	3919.75	-13.40	-0.34	100	1204.71	777.40	427.31	35.46
▶41	3182.29	2441.96	740.33	23.26	▶101	2262.89	1775.34	487.55	21.54
▶42	3338.36	2328.09	1010.27	30.26	▶102	4017.66	3941.84	75.82	1.88
▶43	5065.42	5952.05	-886.63	-17.50	▶103	4262.80	3376.51	886.29	20.79
▶44	2405.33	1719.83	685.50	28.49	▶104	4132.92	4103.04	29.88	0.72
45	2553.61	2570.01	-16.40	-0.64	▶105	1977.72	1394.06	583.66	29.51
▶46	2581.83	2805.29	-223.46	-8.65	106	2701.80	2045.70	656.10	24.28
▶47	2998.31	3142.24	-143.93	-4.80	107	2021.96	1336.03	685.93	33.92
48	2638.95	2529.43	109.52	4.15	▶108	2893.63	2083.63	810.00	27.99
▶49	3232.86	2933.89	298.97	9.24	▶109	2732.79	1966.24	766.55	28.05
▶50	3354.81	2691.30	663.51	19.77	▶110	1748.02	1349.33	398.69	22.80
51	2109.51	1292.48	817.03	38.73	111	1129.85	730.16	399.69	35.37
52	1818.78	919.92	898.86	49.42	112	1205.13	915.41	289.72	24.04
53	2277.26	1032.37	1244.89	54.66	113	1231.56	1668.18	-436.62	-35.45
54	2293.52	877.89	1415.63	61.72	▶114	771.16	935.17	-164.01	-21.26
55	2104.95	900.13	1204.82	57.23	115	1764.72	1084.45	680.27	38.54
56	2345.65	1221.90	1123.75	47.90	116	1948.25	1490.63	457.62	23.48
57	2004.95	592.29	1412.66	70.45	117	1513.88	1530.90	-17.02	-1.12
58	2196.86	768.18	1428.68	65.03	118	120.18	253.18	-133.00	-110.66
59	2033.46	697.85	1335.61	65.68					

Table 2 contains values of critical loads for all grids arranged according their numbers. Centre of each grid is specified by geographical co-ordinates (latitude and longitude) in degrees. Values of precipitation for individual grids are given. Number of representative samples and the selected sample for each particular grid are given. From these two columns we can identify the grids that do not have their own representative sample and also identify samples used for neighbouring grids. When one representative sample is used for the calculation of critical load in an adjacent grid, results differ if there is a difference in precipitation. The next column contains a simplified code of geology for individual grids. If a grid contains two geological units, both codes are included. Characteristics of the geological units are presented on page 12. The last columns of Table 2 contain values of critical loads and exceedances.

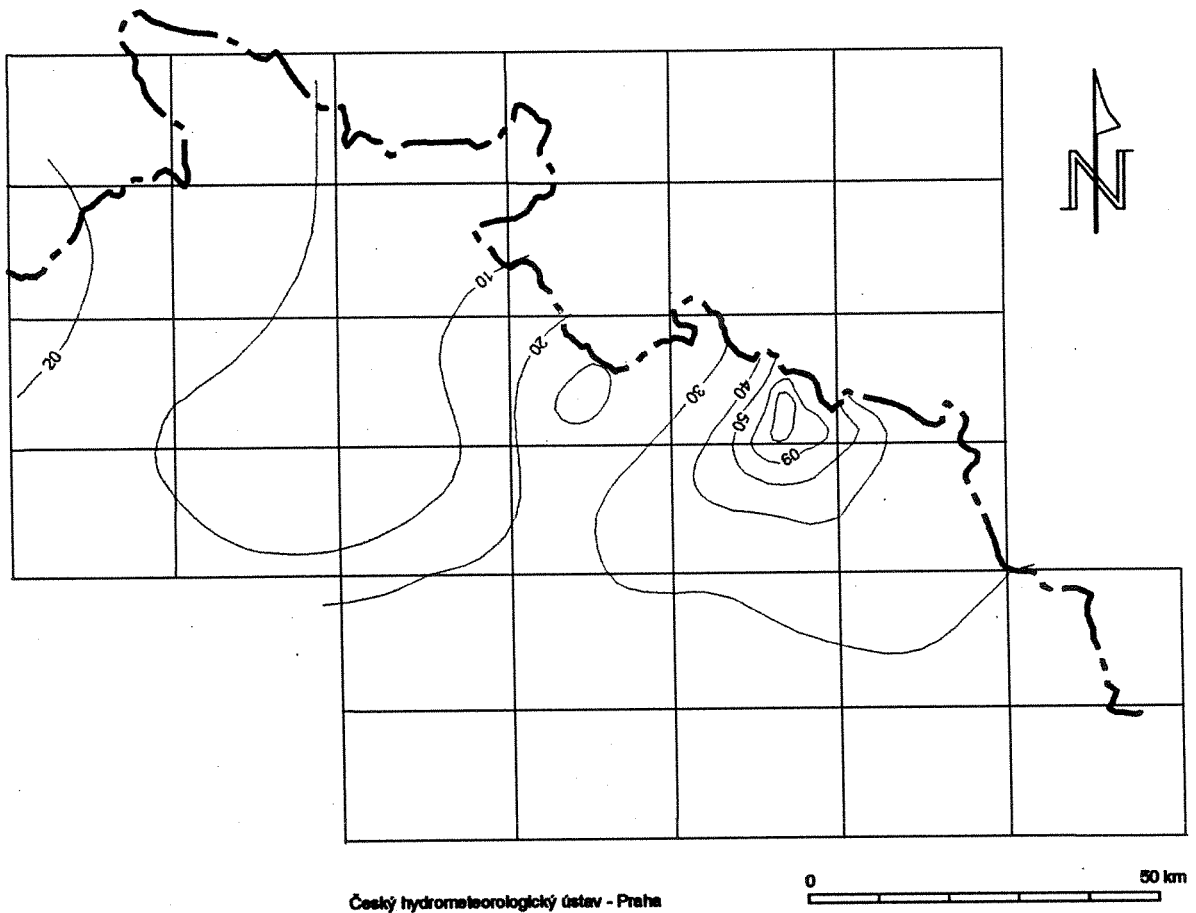


Fig.8. Annual average concentration of SO₂ (ug/m³) in the atmosphere in the study region.

Table 2. The grid number (Fig. 9), centre co-ordinates of the sampling grids, annual precipitation, together with the numbers and the representative sample of each grid, its main geological formation (page 12), and critical load and exceedance of critical load.

Grid	Latit.	Longit.	Precip	Repres. sample	Samples	Geol.	CL keq/km ² /y	CL EX keq/km ² /y
04.434	50.43750	16.91667	700	93	93	1	245	-28
04.443	50.43750	17.08333	700	93		1	245	-28
14.212	50.35139	16.91667	750		92	1		
14.214	50.26528	16.91667	800		98	1		
14.221	50.35139	17.08333	700		96,115	1		
.222	50.35139	17.25000	700	95	94,95	1	1841	-1616
.223	50.26528	17.08333	740	62	62,91,97,116,117	1	1078	-848
.224	50.26528	17.25000	700	90	53,54,90,118	1	670	-435
14.232	50.17917	16.91667	800		99,100	1		
.234	50.09306	16.91667	810			1		
14.241	50.17917	17.08333	790		55,60,61	1		
.242	50.17917	17.25000	960		52,56,57	1		
.243	50.09306	17.08333	780		58,59,72	1		
.244	50.09306	17.25000	980	114	64,65,67,114	1	297	-64
14.412	50.00694	16.91667	790	101	101	1	782	-560
14.421	50.00694	17.08333	780		70,73	1		
.422	50.00694	17.25000	850	69	68,69,71	1,2	600	-369
.423	49.92083	17.08333	730		74	1		
.424	49.92083	17.25000	770	110	110	2,1	665	-437
15.113	50.26528	17.41667	800	89	63	2,1	358	-142
.114	50.26528	17.58333	750	88	88,89	2	720	-500
15.123	50.26528	17.75000	650	103		2	742	-487
15.131	50.17917	17.41667	900	105	51,105,106	2,1	745	-513
.132	50.17917	17.58333	770	87	87	2	815	-585
.133	50.09306	17.41667	850	66	66	2,1	1078	-852
.134	50.09306	17.58333	760	104	104,107	2	1050	-824
15.141	50.17917	17.75000	700	87		2	737	-509
.343	50.09306	17.75000	600	104		2	821	-597
15.311	50.00694	17.41667	770	109		2	820	-594
.312	50.00694	17.58333	750	108	85,108,109	2	1014	-785
.313	49.92083	17.41667	750	83	81,83,112	2	911	-692
.314	49.92083	17.58333	740	79	84	2	1256	-1038
15.321	50.00694	17.75000	540	102	102,103	2	838	-613
.322	50.00694	17.91667	500	42		4	757	-542
.323	49.92083	17.75000	560	78		2	853	-615
.324	49.92083	17.91667	500	42		4	757	-542
15.331	49.83472	17.41667	740		82	2		
.332	49.83472	17.58333	740	79	79	2	1256	-1038
.334	49.74861	17.58333	730		80	2		
15.341	49.83472	17.75000	610	77	48,77,78	2	897	-621
.342	49.83472	17.91667	590	46	45,46	2	554	-341
.343	49.74861	17.75000	680	76	76	2	1042	-792
.344	49.74861	17.91667	630	47	47	2	587	-368
15.411	50.00694	18.08333	500	42	42	4	757	-542
.412	50.00694	18.25000	550			4		
.413	49.92083	18.08333	590	44	44	4,2	374	-150
.414	49.92083	18.25000	630	41	41	4	750	-473
15.423	49.92083	18.41667	650	35		4	816	-593
.424	49.92083	18.58333	660	35		4	830	-606
15.431	49.83472	18.08333	620	49	43,49	2	427	-195
.432	49.83472	18.25000	650	43		4	1212	-962
.433	49.74861	18.08333	660	50		4	481	-233
.434	49.74861	18.25000	680	50	50	4	497	-248
15.441	49.83472	18.41667	680	35	33,34	4	856	-632
.442	49.83472	18.58333	750	35	35	4	948	-723
.443	49.74861	18.41667	760		23,38	3		
.444	49.74861	18.58333	790		36,37	3		
25.122	49.66250	17.91667	650	75		4,2	1620	-1378
25.124	49.57639	17.91667	720	75	32,75	3,4	1800	-1554
25.142	49.49028	17.91667	710		29	3		
25.211	49.66250	18.08333	700	22		3	1791	-1574
.212	49.66250	18.25000	750	19	19,22,39	3	2261	-1962
.213	49.57639	18.08333	750	30	21	3	889	-654
.214	49.57639	18.25000	800	20	20	3	286	-72
25.221	49.66250	18.41667	850	40	40	3	1369	-1154
.222	49.66250	18.58333	900		8	3		
.223	49.57639	18.41667	1100		11	3		
.224	49.57639	18.58333	1070		6,7,9	3		
25.231	49.49028	18.08333	770	30	28,30,31	3	914	-678
.232	49.49028	18.25000	870	17	17,18,25,26,27,111	3	376	-149
.234	49.40417	18.25000	940		24	3		
25.241	49.49028	18.41667	1150	16	12,16,113	3	536	-300
.242	49.49028	18.58333	1100		5,10,13,	3		
.243	49.40417	18.41667	1070	15	14,15	3	495	-272
26.111	49.66250	17.75000	1000		1	3		
.113	49.57639	17.75000	1000		2,3	3		
26.131	49.49028	17.75000	980		4	3		

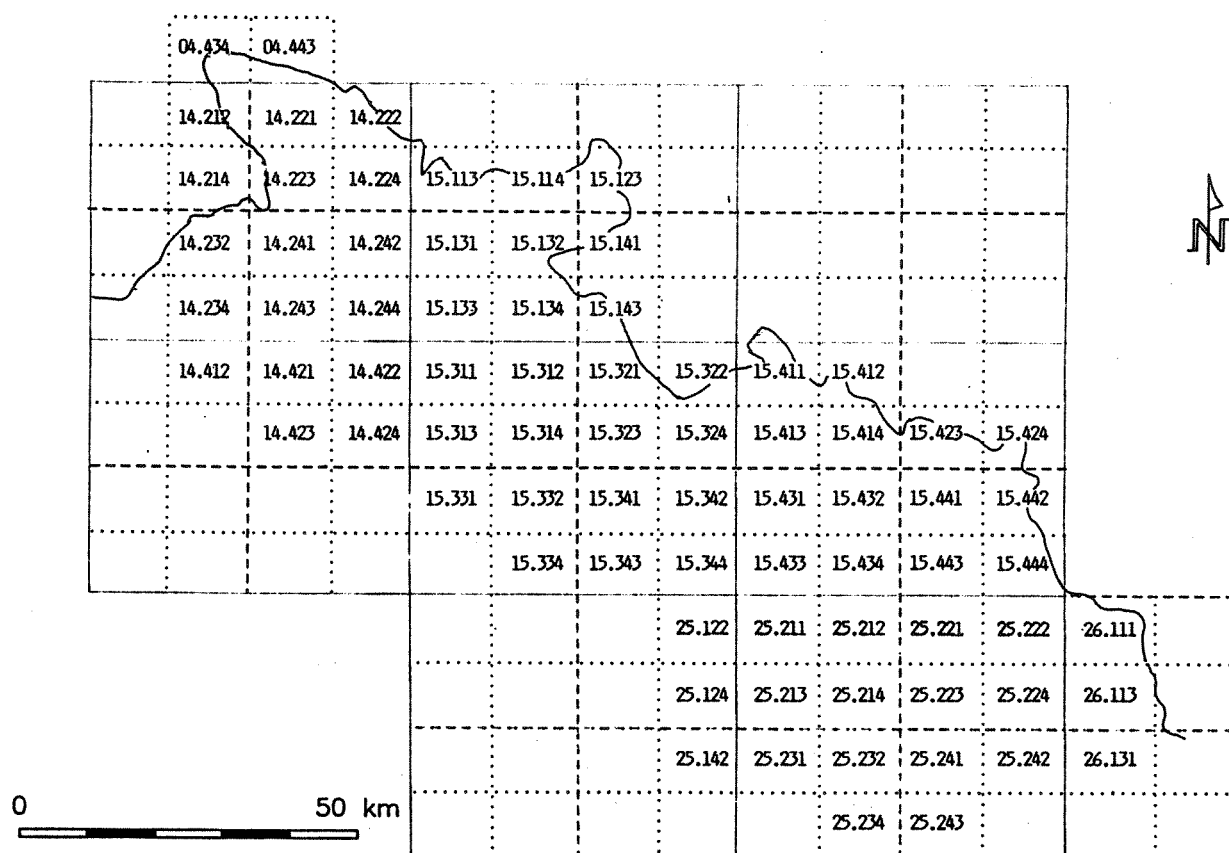


Fig. 9. Numbers of sampling grids using the numbers system of topographical maps.

7.2 MAPS OF CRITICAL LOAD AND EXCEEDANCE

In many parts of the study area there is very limited possibility of obtaining samples which are not contaminated by local sources of pollution like agriculture (fertilizing, livestock) and human settlements. Sampling was restricted to the small streams with the whole catchment covered by forest. In every case an attempt was made to avoid samples with local contamination.

Grid size for the construction of critical load maps should be adjusted to the density of available sampling localities and also to the division of map sheets. Practical reasons have led to the selection of grids which correspond to one quarter of a map sheet in scale 1:50 000. Each grid had a size of 9.5 km by 11.925 (113.29 km²). Maps of scale 1:50 000 were also used for plotting of sample positions and this basic map facilitated further processing. Grids are numbered using the system of map numbering. Numbers of individual grid units are shown in map Fig. 9, and geographical co-ordinates of each grid centre are included in Table 2.

For every grid, selection of representative samples was performed according to its geographical position, geology and chemical balance judged by the water analysis. Selection of suitable chemical samples was performed using a requirement of maximum 30 % difference between concentrations of cations and anions. On the basis of these criteria a representative sample was selected in each grid. In the case of several acceptable samples in one grid, geographical and geological representativity decided the selection of the sample. For a few grids without representative samples, values of suitable samples from an adjacent grid were used. The position of 41 selected samples is illustrated by solid circles in the map of the sampling sites (Fig. 7).

Fig. 10 shows critical loads of acidity (CL) for individual grids. Critical load values are expressed in $\text{keq}/\text{km}^2/\text{year}$ and as $\text{g S}/\text{m}^2/\text{year}$. The colour and scale was chosen to allow expression of the differences within the study area. The scale is shifted to higher values compared to international presentation of critical load. Values of critical loads of surface waters in the whole region are relatively high, which means that they can accept additional acid deposition.

From the total number of 52 grids (Fig. 10), there are 4 grids (approximately 8% of study area) in the lowest class 0 - 300 $\text{keq}/\text{km}^2/\text{year}$. In the group 300 - 600 $\text{keq}/\text{km}^2/\text{year}$ there are 7 grids (13.5 % of study area). A critical load value of zero was found only for one sample (Lake Velke mechove jezirko at Rejviz, grid 14.224). However, this sample was not geologically representative for use in the critical load map.

Critical loads of acidity for forest soils (prepared by Raclavsky and Raclavska) have been compared with values for surface waters. Values of critical loads determined for surface waters are considerably higher than critical loads for soils in the area that has been studied. Average value of critical load of acidity in forest soils in Podbeskydska pahorkatina Upland and in greater part of Nizky Jesenik Mts. were approximately 150 $\text{keq}/\text{km}^2/\text{year}$, and in Moravskoslezske Beskydy Mts. approximately 100 $\text{keq}/\text{km}^2/\text{year}$. In Hruby Jesenik Mts. this value ranges between 0 and 100 $\text{keq}/\text{km}^2/\text{year}$, only exceptionally in some regions (e. g. with amphibolites) can be higher reaching values of 200 $\text{keq}/\text{km}^2/\text{year}$. Values of 100 $\text{keq}/\text{km}^2/\text{year}$ are also probable estimates for eastern part of Hruby Jesenik Mts. and western part of Nizky /Jesenik Mts.

Further studies of surface waters in other regions of The Czech Republic will indicate whether soil or surface water is the most sensitive receptor to acidification in other parts of the country.

Fig. 11 presents the map of exceedance of critical loads of acidity. The units are $\text{keq}/\text{km}^2/\text{year}$ or $\text{g S}/\text{m}^2/\text{year}$. All values are negative, and show that critical load was not exceeded in any of the grids examined. An exception is the Lake Velke mechove jezirko where the value of exceedance was 233 $\text{keq}/\text{km}^2/\text{year}$, but this locality was not used for the map. The group of highest degree of danger (exceedance values between 0 and -300 $\text{keq}/\text{km}^2/\text{year}$) are seen in 11 grids, i. e. approximately 21% of study area (1254 km^2). Two grids will be exceeded with an increase of 10 % of acid deposition, and another two grids with 25 % increase of deposition. 50 % increase of acid deposition will cause exceedance in 7 grids (13%), and a doubling of the acid deposition will cause exceedance of 12 grids (23%). However, lower depositions of acidity are expected in the future.

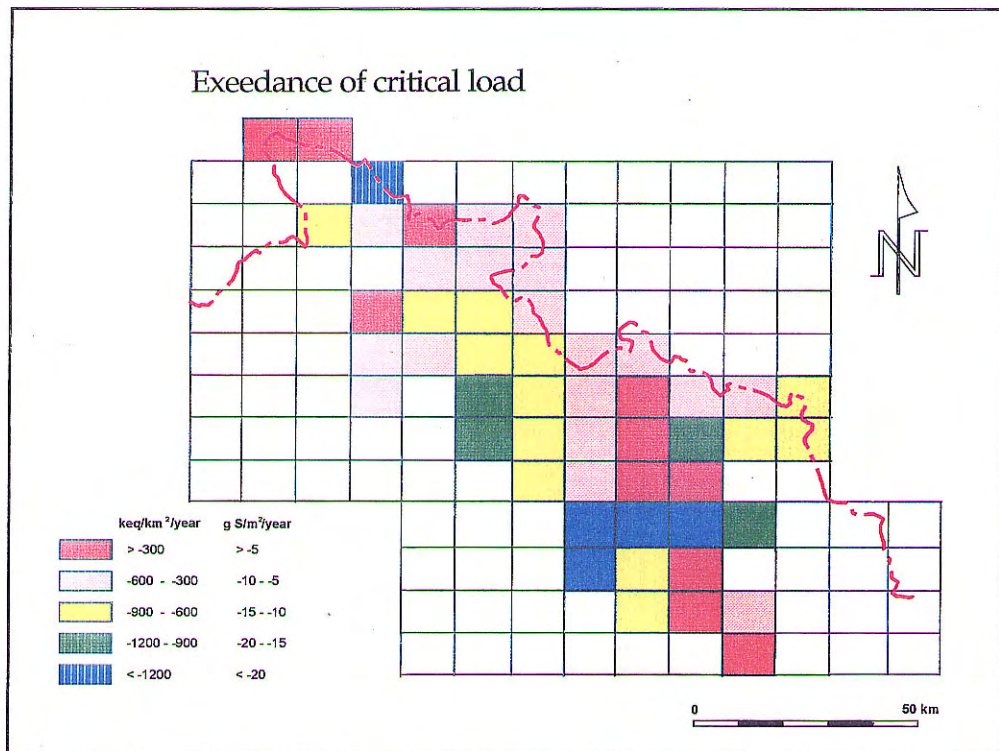
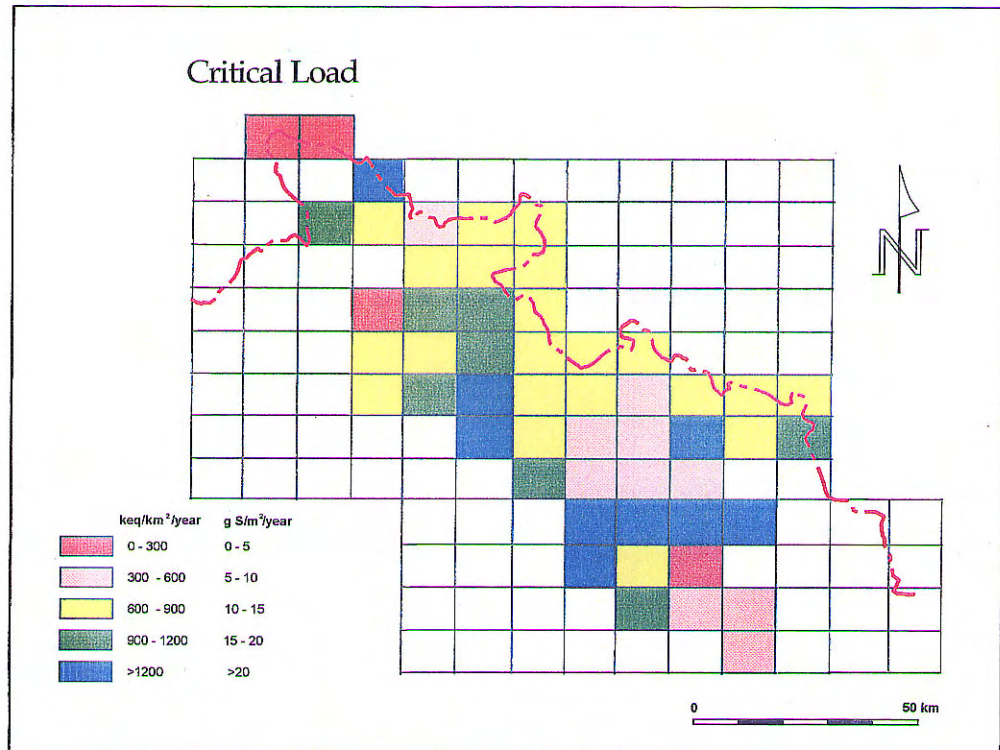


Fig. 10. Map of critical load of acidity to surface waters in northern Moravia and Silesia (above), and Fig. 11. Map of exceedance of critical load of acidity to surface waters (below).

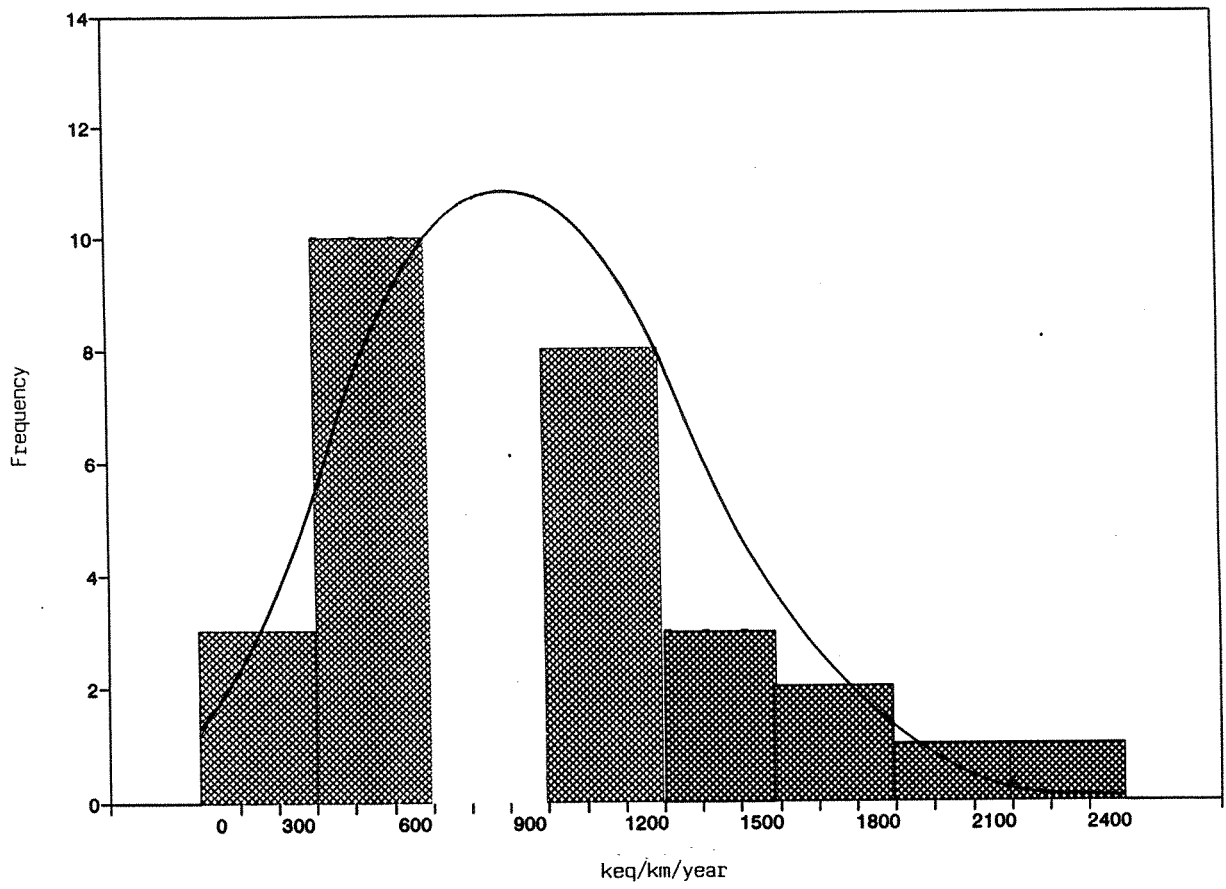


Fig. 12. Frequency distribution of critical load values.

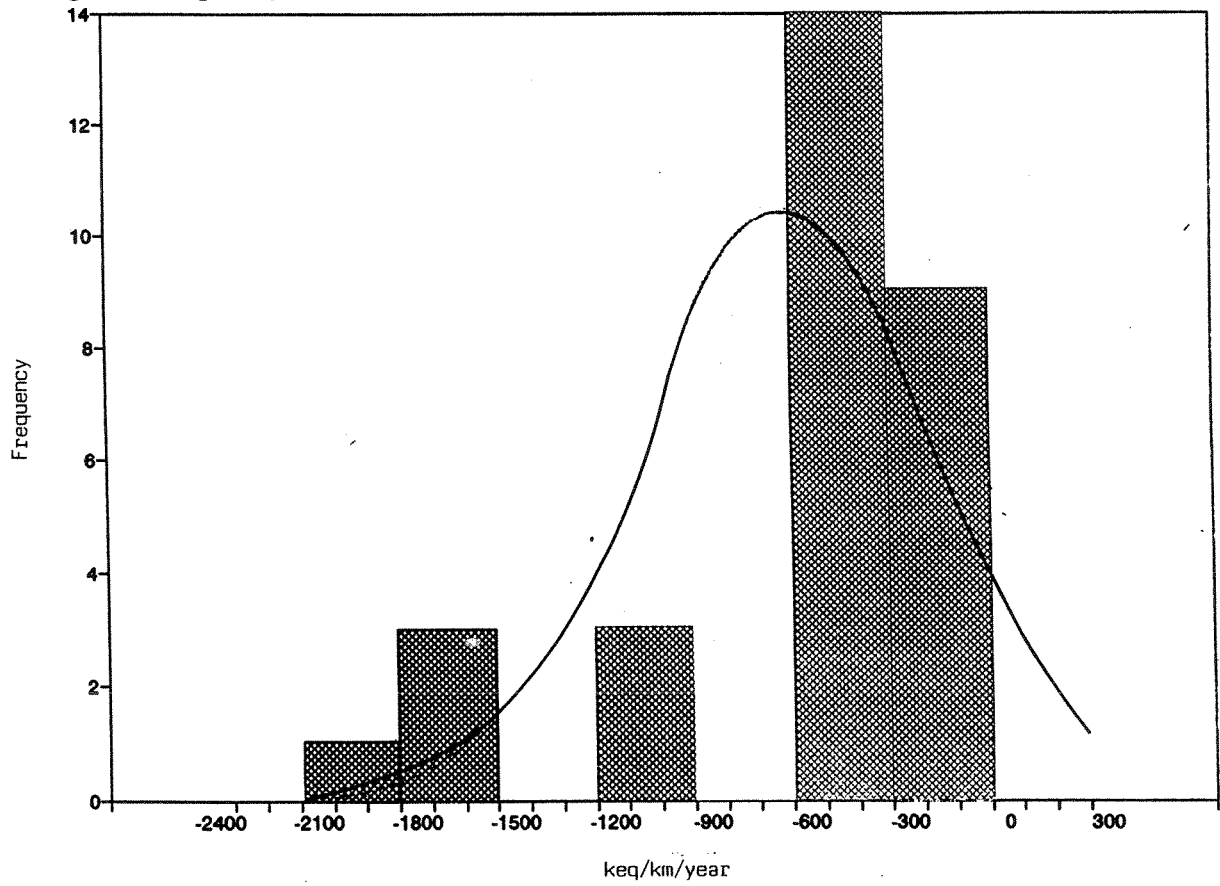


Fig. 13. Frequency distribution of exceedance values of critical loads.

Basic statistical parameters of critical values for the set of 41 selected representative samples are summarized below (units keq/km²/year):

	Critical loads	Exceedances
Average mean	960	- 627
Median	782	- 560
St. deviation	450	444
Minimum value	245	-1962
Maximum value	2261	-28

Distribution of values of critical loads for the different groups is illustrated in Fig. 12. For values of exceedances a similar graph is presented in Fig. 13. The groups correspond to the values in the maps. A wide range and dispersion are seen for values of both critical loads and their exceedance.

8. CONCLUSIONS

High critical loads of acidity to surface waters were calculated for the region of northern Moravia and Silesia. This high critical loads reflect the geological structure of the region. The average value of critical load from this Czech region was approximately twenty times higher than the corresponding value for southern Norway.

Comparing critical loads for soils in parts of the examined region with critical loads for surface waters indicated the lowest critical loads for soils.

Although the deposition of acidifying components in this area was high (5 gS/m²/year compared to 1-2 g in southernmost Norway), no part of the examined region showed exceedance of critical load for surface waters.

Scattered samples of water analyses from several other parts of The Czech Republic indicate both low critical loads and exceedance of critical load in various regions (e.g. Bohemia). The studies of critical loads will therefore continue, and in 1994 the northern Bohemia will be surveyed.

9. REFERENCES

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APPENDIX 1. METHODS OF CHEMICAL ANALYSIS OF WATER SAMPLES

** Sampling and sample conservation*

A. For determination of SO_4^{2-} and Cl^- , samples were taken in 1 litre polyvinyl chloride (PVC) bottles and conserved with 3 ml of chloroform (CnCl) per litre.

B. For aluminium determination samples were taken on 0.5 l PVC bottles and conserved with 5 ml conc. HCl per litre.

C. Samples for total organic carbon (TOC) determination were taken in 0.5 l glass bottles with ground glass stopper. Samples without conservation were delivered for analysis to an external laboratory within 48 hours after sampling.

D. For all other analyses 1.5 l PVC bottles were used without conservation.

After delivery to the laboratory, samples were stored in a refrigerator at 0°C , and all the analysis were done within two or three days.

Most of the analysis were done according to Czech Standard CSN 830520 "Physical and Chemical Analysis of Drinking Water". With exception of turbidity and total organic carbon determination, all analyses were done in the laboratory of the Department of Geology, Mineralogy and Geochemistry at the Mining University in Ostrava (M. Adamusova, Head of the Laboratory).

** pH*

Measuring of pH was done potentiometrically with the pH-metre: WTW-Wissenschaftliche-Technische Werkstätten, Weilheim, type pH 96 with automatic temperature compensation.

** Conductivity*

Conductivity was measured with the conductometre: WTW Weilheim, type LF 96. Conductivity values are in mS/m .

** Turbidity*

Turbidity determination was done in the laboratory of ELCOM Ltd., Ostrava. Analysis was done photometrically according to the Czech Standard CSN 83 0520 (part 34), by comparing sample with basic formazin suspension (Hexamethyltetramin + hydrazinium sulphate) in transmitted light. Turbidity value is in formazine units: $1 \text{ ZF} = 1 \text{ ug SiO}_2/\text{l}$
Detection limit is 0.5 ZF units.

** Dissolved matter*

The amount of dissolved matter (DM) was measured according to the Czech Standard CSN 83 0520 (Part 13) by gravimetric method. After filtration through the membrane filter, Synpor, of pore diameter 0.6 μm the water was evaporated under 105°C and weight of the remnant was determined. The amount of dissolved matter is given as mg/l .

*** *Particulate matter***

Non-dissolved matter (NP) was determined together with dissolved matter by gravimetric method. The membrane filter, Synpor, of 0.6 μm pore diameter, which was used for filtration for dissolved matter was dried under 105 °C and weight increase was determined. The unit of non dissolved matter is mg/l.

*** *Total organic carbon***

Determination of total organic carbon (TOC) was performed by ELCOM Ltd. Ostrava using photometric method on a specialized analyser, Mikrotechna. Concentration of total organic carbon is expressed in mg/l. Limit of detection is 2 mg/l. The laboratory identified too high values for the samples 75, 77, 84 and 85. The results of samples from 75 to 85 are considered not to be reliable.

*** *Alkalinity***

Determination of total alkalinity (Alk 4.5) was performed according to Czech Standard CSN 83 0520 (part 7) using titration by a solution of 0.1 mol/l hydrochloride acid until a pH value of 4.5 with mixed indicator: bromcreosol green and methylene red in methyl alcohol. Values of total alkalinity are expressed in mmol/l.

*** *Sodium and potassium***

Analysis of sodium and potassium was performed by flame photometry with an atomic absorption photometer AAS 3 (Carl Zeis, Jena) in emission mode. Concentration of Na and K is expressed in mg/l.

*** *Calcium***

Determination of calcium was performed according Czech Standard CSN 85 0520 (Part 5) by chelatometric titration using chelaton 3 (bi-natrium salt of diethylamin-tetracetid acid) in alkaline environment (NaOH), and with murexid as an indicator. Concentration of Ca is expressed in mg/l.

*** *Magnesium***

Determination of magnesium was performed from the sum of magnesium and calcium by chelatometric titration using chelaton 3 and eriochrom black as an indicator. From the difference of chelaton consumption during titration for the sum of calcium and magnesium and during titration for calcium alone, the magnesium content is determined. Concentration of Mg is expressed in mg/l.

*** *Aluminium***

Determination of aluminium was performed according the method described by Røgeberg and Henriksen (1985). The analysis distinguishes total monomeric reactive aluminium and monomeric non-labile aluminium which corresponds to Al bound in organic compounds. The determination was performed by photometry on the principle of reaction with pyrocatechine violet at a wavelength of 580 nm. Reactive and non-labile aluminium is separated on an ion-exchange resin (highly acid catex). Concentration of reactive Al and non-labile Al is expressed in $\mu\text{g/l}$.

*** Ammonium**

Determination of ammonium was performed according Czech Standard CSN 83 0520 (Part 19). Photometry with Nessler reagent (complex potassium-mercury iodide) is used in alkaline environment (NaOH) at a wavelength of 400 - 420 nm. The concentration of NH_4 is expressed in mg/l.

*** Chloride**

Determination of chloride was performed according Czech Standard CSN 83 0520 (Part 11) using titration by a solution of silver nitrate AgNO_3 (by argentometry) in neutral environment pH 7 to 10 (without any adjustment) and with phenolphthalein as indicator. Concentration of Cl is expressed in mg/l.

*** Sulphate**

Determination of sulphate was performed by capillary isotachophoresis at an isotachophoretic analyser produced by VILLA, Spisska Nova Ves, Slovakia. A solution of hydrochloric acid, calcium carbonate, beta alanine and polyvinyl alcohol with pH 3.6 was used as a head electrolyte. Citric acid was used as a closing electrolyte. Concentration of sulphate is expressed in mg/l.

*** Nitrate**

Determination of nitrate was performed according Czech Standard CSN 83 0520 (Part 24). Photometry was used on the principle of reaction with sodium salicylate in environment of triacetic acid at the alkaline acidobasic reaction (NaOH). The measurement was performed at a wavelength of 410 nm. Concentration of nitrate is expressed in mg/l.

APPENDIX 2 CHEMICAL ANALYSES

Results of the chemical analyses of water samples: pH, electrical conductivity, turbidity, non-dissolved particles (N.p), dissolved matter (D.m.), TOC, Ca²⁺, Mg²⁺, Na⁺, K⁺, Al_r, Al_{il}, NH₄⁺, Cl⁻, SO₄²⁻, NO₃⁻, and alkalinity.

Sample number	pH	Conduct. mS/m	Turb. ZF	N.p. mg/l	D.m. mg/l	TOC mg/l	Ca	Mg	Na	K	Al _r	Al _{il}	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	ALK mmol/l
							mg/l				µg/l		mg/l				
1	7.16	29.00	0.60	34.00	200.00	2.00	50.10	3.04	1.40	1.30	6.0	1.8	0.130	5.32	46.00	0.000	2.75
2	7.24	18.00	1.70	2.00	130.00	2.00	24.05	1.82	1.50	2.00	9.0	3.4	0.000	7.09	36.13	1.640	1.70
3	7.27	15.00	0.50	6.00	100.00	2.00	18.04	0.61	2.60	1.70	55.0	9.2	0.000	3.54	40.85	0.260	1.15
4	7.04	27.00	0.50	8.00	180.00	2.00	36.07	3.65	8.00	4.10	120.0	27.5	0.120	3.54	35.70	2.180	2.85
5	7.16	13.00	0.50	29.00	40.00	2.00	16.03	2.43	1.00	1.70	175.0	41.0	0.000	3.54	28.83	1.220	1.05
6	7.16	11.00	0.50	15.00	60.00	2.00	16.03	1.22	0.60	0.80	2.0	0.5	0.000	1.77	26.26	1.050	1.00
7	7.20	9.00	0.50	10.00	70.00	2.00	12.02	0.61	0.50	0.00	68.0	11.2	0.000	3.54	26.26	1.850	0.75
8	7.05	13.00	5.00	15.00	90.00	2.00	16.03	1.82	0.80	1.30	89.0	26.3	0.000	4.43	32.27	2.740	0.90
9	7.08	14.00	0.60	7.00	80.00	2.00	19.04	0.61	0.70	1.30	58.0	11.2	0.000	3.54	23.68	2.440	1.10
10	7.08	16.00	0.50	17.00	150.00	2.00	22.04	4.86	1.60	1.70	34.0	7.8	0.000	5.32	34.84	0.520	1.40
11	7.24	11.00	0.50	11.00	90.00	2.00	15.03	1.22	0.60	1.30	98.0	42.3	0.000	2.66	23.68	1.960	0.60
12	7.13	15.00	0.50	3.00	110.00	2.00	20.04	1.22	1.10	1.70	7.0	0.5	0.000	4.43	21.96	1.990	1.55
13	7.16	13.00	0.50	7.00	70.00	2.00	15.03	2.43	1.50	2.00	1.0	0.0	0.000	3.54	13.38	0.790	1.25
14	7.12	14.00	0.50	11.00	100.00	2.00	16.03	3.04	1.20	2.00	64.0	18.4	0.000	4.43	17.67	2.060	0.70
15	7.13	12.00	0.50	10.00	100.00	2.00	13.03	3.04	1.30	2.00	563.0	121.5	0.160	2.66	12.52	0.970	0.85
16	7.20	11.00	0.50	1.00	90.00	2.00	14.03	3.04	0.40	1.30	111.0	37.4	0.000	2.66	12.95	1.900	0.75
17	7.16	11.00	0.50	3.00	70.00	2.00	15.03	1.22	0.40	0.80	46.0	19.6	0.000	2.66	10.37	1.540	0.75
18	7.16	11.00	0.60	2.00	90.00	2.00	14.03	0.61	0.50	1.30	8.0	0.2	0.000	3.54	12.52	1.570	0.80
19	6.65	47.00	0.50	6.00	320.00	2.00	83.17	9.12	0.50	1.70	5.0	0.3	0.000	7.09	28.83	5.030	4.50
20	7.16	13.00	1.70	2.00	50.00	2.00	15.03	0.61	1.10	1.70	9.0	1.2	0.000	3.54	15.95	0.140	0.60
21	6.61	53.00	5.20	65.00	310.00	2.00	33.07	34.66	5.00	3.70	6.0	0.8	0.270	6.20	67.65	0.170	5.85
22	6.81	52.00	0.50	7.00	290.00	7.20	68.14	7.30	17.00	70.00	7.0	0.9	0.200	15.95	125.85	0.610	2.55
23	5.70	19.00	0.50	5.00	164.00	2.00	17.03	7.90	5.00	2.00	498.0	121.2	0.210	9.75	79.63	1.810	0.40
24	6.19	14.00	0.50	21.00	90.00	2.00	19.04	2.43	1.30	1.70	7.0	8.4	0.190	3.54	25.17	0.260	1.35
25	6.41	13.00	0.50	6.00	65.00	2.00	19.04	1.22	0.40	1.30	5.0	1.9	0.090	2.66	23.98	1.140	1.05
26	6.45	12.00	0.60	1.00	74.00	2.00	13.03	2.43	1.30	1.30	1.0	0.6	0.130	3.54	34.65	0.190	0.65
27	6.59	14.00	0.80	3.00	106.00	2.00	19.04	2.43	0.40	0.80	5.0	1.2	0.100	2.66	21.61	0.380	1.15
28	6.78	24.00	0.50	5.00	142.00	2.00	31.06	4.26	5.00	2.60	61.0	14.8	0.180	5.32	46.51	0.940	1.75
29	7.22	60.00	0.50	43.00	394.00	28.70	28.06	40.13	25.00	6.90	7.0	1.7	0.450	9.75	73.77	0.240	6.35
30	6.85	29.00	0.50	28.00	198.00	2.00	31.06	9.12	12.00	3.40	1.0	0.0	0.440	6.20	45.64	2.760	2.50
31	6.89	14.00	0.60	3.00	112.00	2.00	18.04	3.04	0.60	1.70	35.0	12.3	0.110	5.32	24.96	0.460	1.05
32	7.03	70.00	0.50	114.00	455.00	36.20	30.06	39.52	18.00	4.10	37.0	11.4	0.290	8.86	97.34	0.460	6.85
33	7.07	1.36	0.50	6.00	1048.00	18.80	99.20	81.47	54.00	30.00	74.0	23.0	0.720	103.69	538.40	1.680	4.15
34	6.34	15.00	0.70	74.00	142.00	2.00	13.03	6.69	1.40	1.70	222.0	126.4	0.250	6.20	58.80	1.240	0.40
35	7.07	45.00	0.50	22.00	317.00	2.00	64.13	9.73	9.00	3.70	237.0	45.5	0.460	23.04	106.74	1.570	2.95
36	6.78	16.00	0.70	0.00	120.00	2.00	13.03	4.26	5.00	1.70	7.0	5.6	0.130	7.98	62.56	0.400	0.75
37	6.82	17.00	0.60	30.00	112.00	2.00	21.04	3.04	3.00	2.00	7.0	1.3	0.500	7.09	43.76	0.240	1.55
38	6.78	22.00	1.00	35.00	156.00	2.00	20.04	9.12	4.00	2.00	31.0	9.7	0.610	10.63	92.64	1.290	0.70
39	7.22	68.00	7.00	12.00	226.00	15.60	60.12	17.02	8.00	7.00	71.0	12.4	0.320	11.52	34.36	2.530	4.50
40	7.24	33.00	1.00	26.00	189.00	2.00	46.09	11.55	9.00	9.00	446.0	171.5	0.530	22.16	54.80	0.310	2.15
41	7.06	32.00	1.90	9.00	229.00	2.00	35.07	7.90	13.00	8.00	9.0	3.2	0.150	37.22	33.41	9.140	0.55
42	7.10	20.00	3.20	15.00	162.00	2.00	23.05	19.46	8.00	7.00	951.0	276.2	1.030	9.75	35.79	0.540	1.30
43	6.91	52.00	6.60	18.00	324.00	29.80	48.10	17.02	22.00	11.00	49.0	11.8	0.380	36.34	54.80	5.420	3.70
44	7.03	23.00	0.50	6.00	133.00	2.00	22.04	9.73	7.00	7.00	18.0	5.4	0.340	9.75	54.22	1.060	0.30
45	7.10	25.00	2.30	33.00	143.00	2.00	25.05	9.73	7.00	7.00	65.0	14.9	0.300	2.66	44.58	1.100	1.55
46	7.18	25.00	0.50	6.00	214.00	2.00	26.05	9.73	6.00	8.00	92.0	61.8	0.230	6.20	46.99	0.190	1.65
47	6.99	28.00	0.50	10.00	166.00	2.00	35.07	9.12	7.00	7.00	55.0	45.4	0.190	10.63	61.44	0.900	1.55
48	7.06	26.00	0.50	5.00	150.00	2.00	31.06	6.69	7.00	8.00	46.0	11.2	0.470	14.18	67.50	2.080	0.90
49	7.06	31.00	0.50	9.00	164.00	2.00	28.06	15.81	7.00	8.00	6.0	1.7	0.350	15.07	87.13	2.890	0.65
50	6.55	32.00	0.50	2.00	69.00	2.00	37.07	10.34	10.00	8.00	83.0	35.4	0.190	12.41	87.13	4.900	0.45

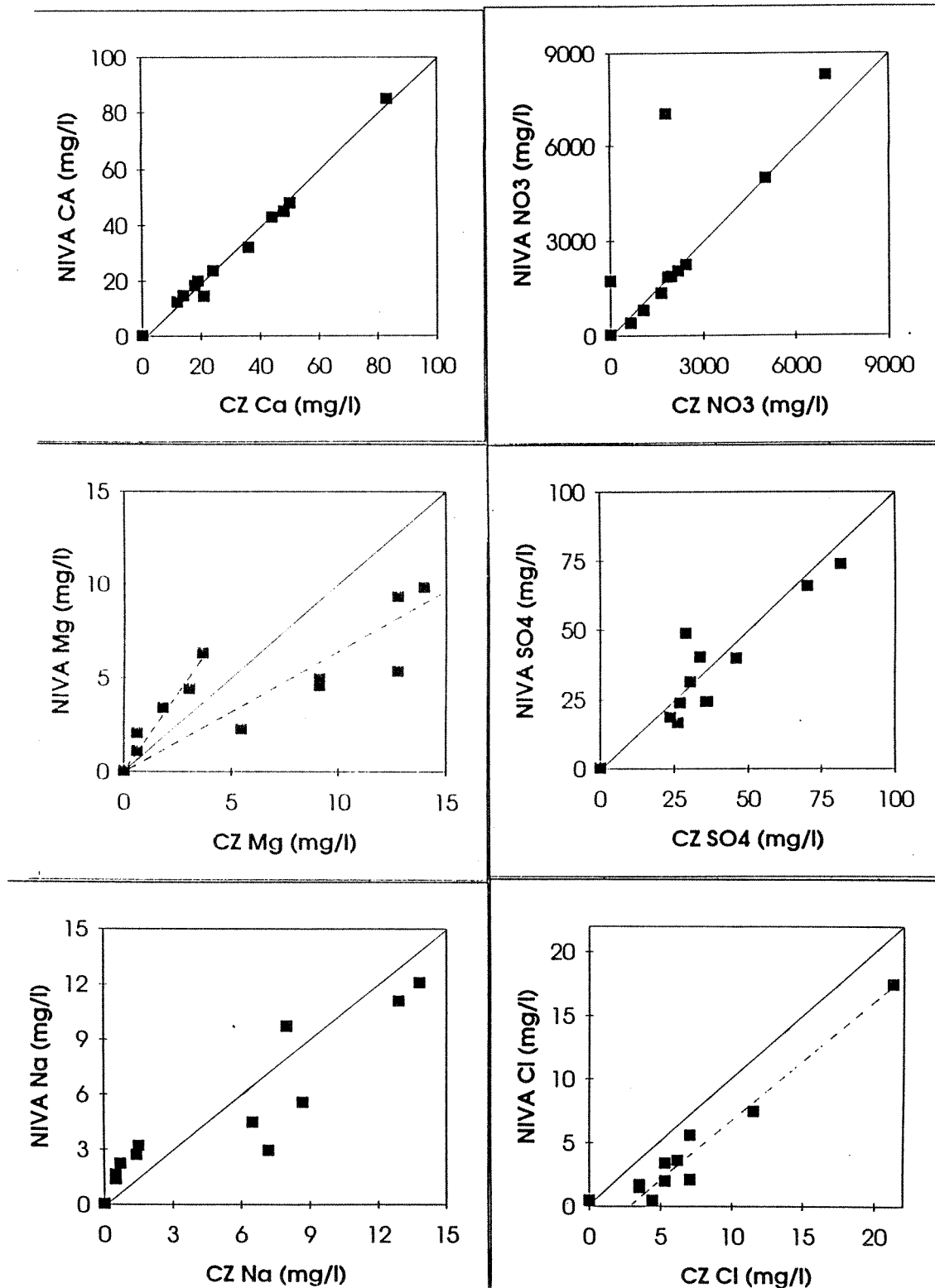
Appendix 2 continued

Sample number	pH	Conduct.	Turb.	N.p.	D.m.	TOC	Ca	Mg	Na	K	Al _r	Al _{il}	NH ₄ ⁺	Cl ⁻	SO ₄ ⁻²	NO ₃ ⁻	ALK
		mS/m	ZF	mg/l	mg/l	mg/l	mg/l				µg/l		mg/l			mmol/l	
51	7.55	12.00	0.60	2.00	81.00	7.90	15.03	11.55	5.60	6.40	6.0	1.9	0.000	5.32	19.69	2.040	0.70
52	7.22	9.00	0.70	3.00	56.00	6.10	14.03	8.51	5.70	6.60	31.0	18.4	0.000	4.43	14.88	2.200	0.45
53	7.51	12.00	0.70	7.00	69.00	7.00	15.03	13.38	5.70	6.90	378.0	211.8	0.000	3.54	14.08	2.460	0.60
54	7.37	7.00	0.50	3.00	54.00	8.60	14.03	13.98	6.00	6.40	5.0	1.2	0.300	4.43	6.85	0.650	0.60
55	7.22	8.00	0.80	9.00	69.00	6.00	16.03	10.94	5.50	6.40	24.0	9.6	0.000	4.43	16.48	2.010	0.40
56	7.37	11.00	0.60	3.00	76.00	10.60	14.03	14.59	5.70	6.40	5.0	4.2	0.570	3.54	21.30	1.800	0.65
57	7.22	7.00	0.70	7.00	61.00	4.70	14.03	10.94	5.50	6.40	6.0	3.7	0.000	0.88	13.27	2.570	0.25
58	7.34	8.00	0.60	2.00	72.00	9.60	15.03	12.77	5.30	6.40	126.5	81.2	0.000	0.00	14.08	1.570	0.45
59	7.04	9.00	0.80	3.00	75.00	3.70	15.03	10.34	6.20	6.30	135.0	45.6	0.000	3.54	17.29	2.380	0.20
60	7.07	9.00	0.70	3.00	93.00	9.70	16.03	13.98	6.80	6.40	101.0	37.2	0.090	0.88	21.30	2.050	0.35
61	7.33	11.00	0.70	3.00	107.00	9.20	15.03	12.77	5.50	6.40	322.6	181.7	0.100	2.66	21.30	2.630	0.45
62	7.74	16.00	0.90	2.00	114.00	20.00	24.05	12.77	5.40	6.40	285.7	175.6	0.000	2.66	19.70	2.160	1.45
63	7.29	17.00	0.80	3.00	128.00	11.40	26.05	10.94	5.90	6.60	273.4	136.4	0.140	3.54	14.37	2.150	0.80
64	6.37	9.00	0.90	5.00	104.00	7.10	12.02	6.69	5.90	6.80	196.7	68.5	0.000	0.88	13.42	1.350	0.30
65	7.07	8.00	0.70	1.00	71.00	8.40	14.03	5.47	5.40	6.40	218.2	171.5	0.000	1.77	11.50	1.570	0.45
66	7.62	15.00	0.90	4.00	98.00	20.80	21.04	10.34	5.60	6.40	22.0	5.6	0.000	2.66	17.24	1.460	1.25
67	7.07	7.00	0.70	2.00	57.00	13.10	9.02	10.34	5.00	6.30	68.0	23.7	0.000	1.77	7.68	1.420	0.50
68	7.37	7.00	1.00	2.00	47.00	13.80	14.03	6.08	4.90	6.40	5.7	2.4	0.000	1.77	9.59	2.080	0.55
69	7.44	8.00	0.80	9.00	61.00	13.00	12.02	6.69	5.10	6.40	101.6	41.8	0.000	0.88	20.77	1.970	0.70
70	7.25	13.00	0.50	9.00	81.00	18.30	19.04	17.02	6.30	6.60	86.3	53.6	0.830	2.66	22.15	1.990	0.75
71	7.18	8.00	0.50	2.00	84.00	16.10	18.04	10.94	5.10	6.40	340.9	141.8	0.000	3.54	13.83	2.010	0.55
72	6.96	11.00	0.70	6.00	91.00	26.90	18.04	8.51	7.10	6.40	469.8	271.2	0.000	2.66	28.39	2.580	0.30
73	7.59	14.00	0.50	7.00	146.00	29.00	31.06	6.08	8.20	6.80	141.5	38.6	0.460	1.77	26.31	0.860	0.95
74	7.37	12.00	0.70	3.00	93.00	30.90	27.05	13.98	6.60	6.30	70.9	29.2	0.000	2.66	17.99	1.370	1.05
75	7.44	37.00	0.50	7.00	299.00	125.00	60.12	7.90	11.10	6.60	58.7	35.1	0.170	3.54	24.93	4.130	3.40
76	6.89	29.00	0.50	10.00	232.00	34.00	38.08	17.63	8.70	6.40	620.2	195.4	0.020	11.52	59.91	4.900	0.95
77	7.25	41.00	0.70	4.00	339.00	30.30	45.09	19.46	11.70	9.00	491.3	311.2	0.030	26.59	85.00	9.310	0.70
78	7.37	30.00	0.60	5.00	141.00	54.80	28.06	20.67	11.90	7.30	12.3	6.7	0.020	27.47	56.01	3.730	1.25
79	7.74	29.00	0.60	6.00	192.00	68.00	37.07	17.02	9.50	9.20	307.2	201.5	0.000	8.86	56.01	0.740	2.00
80	7.06	16.00	0.60	2.00	255.00	59.00	29.06	9.73	6.90	6.30	40.3	20.7	0.000	7.09	47.09	1.600	0.35
81	7.29	11.00	0.50	3.00	97.00	95.10	13.03	15.20	6.90	6.30	0.5	0.0	0.130	5.32	25.90	0.420	0.45
82	7.10	11.00	0.50	2.00	83.00	92.90	14.03	13.98	7.00	6.40	98.6	75.4	0.000	7.09	23.67	0.390	0.55
83	7.74	15.00	0.60	23.00	112.00	94.50	19.04	12.77	7.60	6.40	669.3	397.1	0.000	7.29	23.67	0.860	1.30
84	7.71	14.00	0.60	1.00	100.00	130.00	15.03	30.40	9.20	6.60	313.3	191.2	0.100	5.32	16.98	0.430	1.30
85	7.37	23.00	0.50	2.00	151.00	141.00	27.05	17.02	12.40	6.80	156.8	98.7	0.000	15.95	33.71	1.620	1.20
87	7.18	27.00	0.50	3.00	208.00	3.50	22.04	20.67	9.10	7.90	107.8	67.8	0.430	9.75	73.65	2.100	1.10
88	7.65	28.00	0.50	14.00	204.00	14.90	11.02	18.85	10.70	8.00	561.9	391.2	3.760	9.75	50.86	1.060	2.05
89	7.15	18.00	0.60	1.00	92.00	2.00	17.03	9.12	7.50	0.00	304.1	192.4	0.300	6.20	48.68	0.530	0.45
90	7.26	17.00	0.80	3.00	109.00	2.00	28.06	6.69	5.30	0.00	239.7	65.2	0.000	7.09	24.80	2.850	1.15
91	7.33	12.00	0.70	1.00	88.00	2.00	14.03	10.34	6.20	7.70	282.7	128.4	0.050	4.43	30.29	2.210	0.55
92	5.67	11.00	0.50	4.00	96.00	2.00	27.05	3.04	7.40	0.00	175.3	151.2	0.490	5.32	43.26	0.440	0.15
93	6.97	15.00	0.60	1.00	52.00	2.00	12.02	10.34	7.90	0.00	331.8	287.2	0.560	6.20	50.86	0.480	0.45
94	6.53	9.00	0.60	4.00	157.00	2.00	11.02	6.08	7.20	0.00	304.2	101.1	0.310	4.43	18.42	0.490	0.25
95	7.62	39.00	0.50	9.00	1904.00	19.00	69.14	14.59	9.00	7.90	328.7	195.6	0.120	15.07	49.01	1.670	2.70
96	6.53	17.00	0.50	4.00	186.00	2.00	13.03	13.34	10.40	7.80	338.0	172.3	0.700	7.98	48.47	0.000	0.15
97	7.22	9.00	0.60	3.00	72.00	2.00	11.02	7.30	6.50	0.00	831.9	618.4	0.230	4.43	16.24	0.870	0.40
98	7.44	8.00	0.70	2.00	70.00	2.00	11.02	6.69	5.80	0.00	724.5	369.3	0.140	4.43	14.05	0.710	0.35
99	7.18	5.00	0.00	4.00	61.00	2.00	6.01	3.65	6.30	0.00	338.0	185.4	0.090	4.43	8.59	1.740	0.20
100	5.31	8.00	0.90	1.00	62.00	2.00	14.03	3.04	5.60	0.00	1991.7	1005.0	0.170	4.43	19.52	2.880	0.20
101	6.97	16.00	0.50	7.00	111.00	2.00	18.04	12.77	6.50	0.00	101.2	38.2	0.490	4.43	30.44	1.070	1.00
102	7.70	33.00	0.50	3.00	259.00	36.90	38.08	12.77	16.60	12.20	141.5	79.6	0.510	15.95	58.14	2.030	2.25
103	6.70	35.00	0.60	5.00	288.00	33.80	48.10	12.77	13.80	6.40	71.7	65.0	0.770	21.27	70.39	6.980	1.20
104	7.77	32.00	0.50	13.00	245.00	22.40	44.09	13.98	12.90	6.30	101.3	31.2	1.000	11.52	81.69	1.800	2.05
105	7.78	11.00	0.70	1.00	84.00	2.00	21.04	5.47	7.20	5.80	150.2	73.8	0.250	5.32	27.04	1.960	0.65
106	7.99	17.00	0.90	7.00	143.00	6.30	24.05	12.16	7.30	5.90	201.2	154.7	0.540	7.09	11.97	2.900	1.55
107	7.54	14.00	0.60	4.00	125.00	2.00	14.03	9.12	8.70	6.20	5.0	1.2	0.590	6.20	33.68	0.660	0.45
108	7.81	20.00	0.50	1.00	168.00	10.70	24.05	12.77	10.30	6.40	165.3	78.3	0.510	5.32	33.68	2.050	1.20
109	7.22	18.00	0.70	1.00	141.00	2.00	23.05	12.16	9.50	6.30	178.0	125.1	0.090	7.09	42.75	1.680	0.85
110	7.70	9.00	0.80	1.00	64.00	2.00	14.03	6.69	7.50	6.00	241.0	191.8	0.290	5.32	12.94	1.870	0.90
111	7.55	12.03	0.00	0.00	0.00	1.50	17.60	1.87	1.67	0.91	210.0	10.0	0.000	2.00	17.00	2.800	0.27
112	5.95	14.02	0.00	0.00	0.00	8.30	13.30	3.75	3.99	1.18	218.0	20.0	0.500	3.50	35.50	1.135	0.06
113	7.63	13.36	0.00	0.00	0.00	1.80	17.10	2.75	2.72	1.24	10.0	10.0	0.003	1.20	22.00	1.720	1.14
114	7.26	8.77	0.00	0.00	0.00	1.30	10.01	1.52	2.61	1.24	10.0	10.0	0.005	0.80	16.00	1.910	0.54
115	6.90	9.00	0.70	11.00	65.00	13.20	11.02	7.30	5.90	8.20	546.0	237.8	2.640	4.43	0.00	0.590	0.95
116	6.86	11.00	1.50	5.00	71.00	2.00	13.03	7.90	7.00	8.10	291.8	135.4	2.430	4.43	19.52	0.600	0.95
117	7.58	14.97	0.00	0.00	0.00	3.90	20.50	2.22	3.92	5.00	15.0	10.0	0.138	3.50	12.00	0.037	1.18
118	3.86	7.16	0.00	0.00	0.00	16.50	1.39	0.34	0.32	0.07	156.0	72.0	0.126	1.60	10.00	0.004	0.00

APPENDIX 3 INTERCALIBRATION

65 % of water samples analysed in The Czech Republic showed deviations of more than 30 % between cations and anions. These samples were therefore not acceptable for calculation of critical loads. 12 samples including one blank control were re-analysed at NIVA. The comparison between calcium, magnesium, sodium, nitrate, sulphate and chloride are shown below.

Excellent correlation was seen for calcium, and quite good agreements occurred for sodium, sulphate, and with a few exceptions also for nitrate. Chloride was systematically higher in the Czech analysis while magnesium showed both higher and lower values.



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