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

Critical loads of acidity
to surface waters,
north-eastern Bohemia
and northern Moravia,
The Czech Republic



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Abstract: **Critical loads of acidity to surface waters and their exceedances were estimated for north-eastern Bohemia and Moravia in The Czech Republic. 13 400 km² or 17 % of the area of the country has been surveyed. Varying critical loads were observed within the examined region. 19 % of the examined area showed exceedance of critical load, and an other 11 % was close to exceedance. A continuation of the survey is recommended in Bohemia.**

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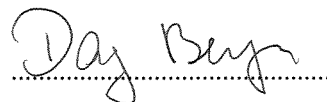
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For the Administration



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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,
NORTH-EASTERN BOHEMIA AND NORTHERN MORAVIA,
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, Technical University, Ostrava (TUO), and Povodi Odry (PO) to execute several projects under the programme area "Abatement strategies in the River Odra catchment".

As part of the project was defined: "Assessing critical loads of acidity to surface waters in The Czech Republic." The project started in the region of northern Moravia in 1993 and continued in north-eastern Bohemia in 1994. The project was supported by grants from The Ministry of Environment of The Czech Republic, The Norwegian Ministry of Environment, Technical University, Ostrava, and Norwegian Institute for Water Research (NIVA). The project is a co-operation of the Norwegian Institute for Water Research (NIVA) and the Technical University, Ostrava (TUO).

Oslo, January 1996.

Leif Lien

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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 to 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 north-eastern Bohemia and northern Moravia, 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.

Inter-comparison of 81 water analyses between Technical University, Ostrava and Norwegian Institute for Water Research showed, with a few exceptions (pH, chloride), acceptable agreements for 10 parameters.

Approximately 13 400 km², or 17 % of the total area of the Czech Republic, have been examined for critical load and exceedance. The deposition of acidifying sulphur components in this part of Europe is high (5 gS/m²/year compared to 1-2 g in South Norway). 2.500 km² or 19 % of the examined area showed exceedance of critical load, and another 1.500 km² (11 %) was close to exceedance. Parts of this area were probably exceeded some years ago when the deposition of sulphur was higher. Due to a conservative calculation of critical load and exceedance some of this area might still be exceeded.

The calculated values of exceedance show high negative figures for other parts of the region, e.g. northern Moravia, indicating that they can tolerate higher acid deposition.

Scattered water samples from several other parts of The Czech Republic indicate both low critical loads and exceedances of critical load in various regions (e.g. Bohemia). The studies of critical loads should therefore be continued in these regions.

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 numerous acidic and fishless lakes in the 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 soil and for surface water have been worked out (Sverdrup et al. 1990). Critical loads of acidity and the exceedances for sulphur and nitrogen to surface waters were first mapped for Norway, and a project under the Nordic Council of Ministers has mapped critical loads and their exceedance for surface waters in 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 that 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 freshwater use chemical data. The critical chemical value is based on knowledge of the ecological tolerance of sensitive biological species to changes in water chemistry. Resistibility 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.

The steady-state water chemistry method

Acid Neutralisation 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 in order 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:

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

In north-eastern Bohemia and Moravia the occurrence of chloride in the surface water was mainly expected to be of local geological origin, and the sea salt import of marine origin was neglectable. The pre-industrial non-marine base cation concentration for north-eastern Bohemia and Moravia was therefore 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, $SO_4^*_{dep}$

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

Fish was selected as a biological indicator for a critical value of ANC (Lien et al. 1995). 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. 1995). 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: NORTH-EASTERN BOHEMIA AND NORTHERN MORAVIA

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 were 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).

Sampling continued in 1994 in the north-eastern Bohemia. This is located north-west of the former studied area, limited by the Czech - Polish border in north and north-east, and a line Zabreh - Rychnov nad Kneznou - Dvur Kralove - Liberec in south and south- west (Fig. 1 and 2).

The sampling area includes from east to west the following geographical units. The eastern part of the studied territory belongs to Western Carpathians: Podbeskydska pahorkatina Hills and Moravskoslezske Beskydy Mts. A small area east of Moravskoslezske Beskydy Mts. is part of Slezske Beskydy Mts. The boundary with Bohemian Massif is formed by the depression of the Moravian Gate, which passes into Ostrava Basin. Nizky Jesenik Mts. (Low Jesenik) and Oderske vrchy (Odra Hills) form a hilly area between Moravian Gate and Hruby Jesenik Mts (High Jesenik). North of Hruby Jesenik Mts. is the small area of Rychlebske Hory Mts. located, and in west is the Kralicky Sneznik Mt. Farther to the west follow the Orlicke Hory Mts. (Eagle Mts.) and Broumovske mezihori (Broumov Hills). West of these mountains is the large territory of Krkonose Mts. (Giant Mts.) with highest point in the Czech Republic - Snezka (1602 m a.s.l.). The sampled area partly reaches Jizerske Hory (Jizera Mts.) west of Krkonose Mts.

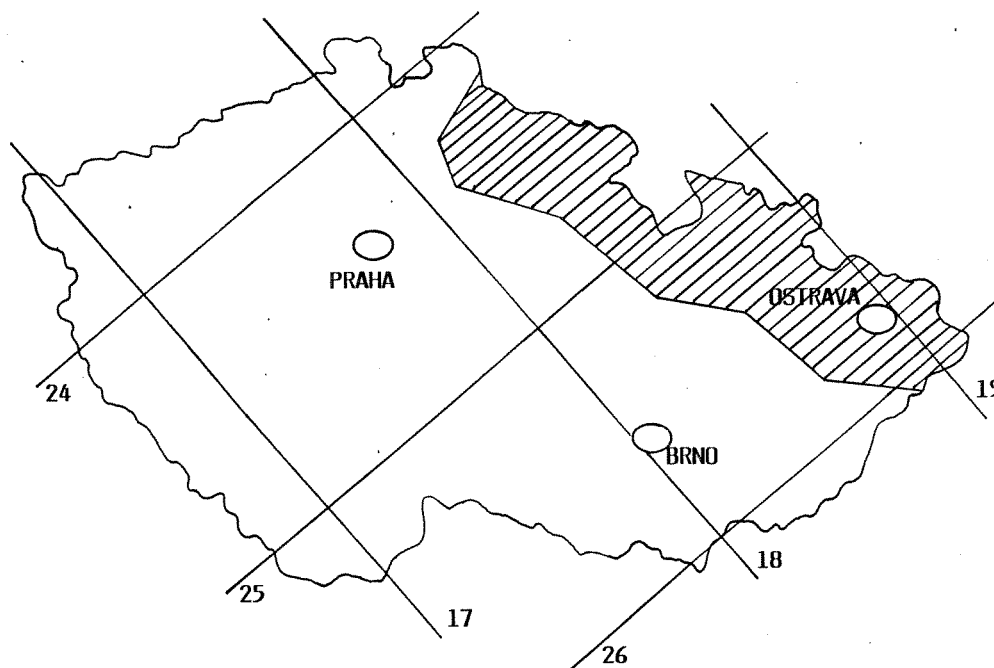


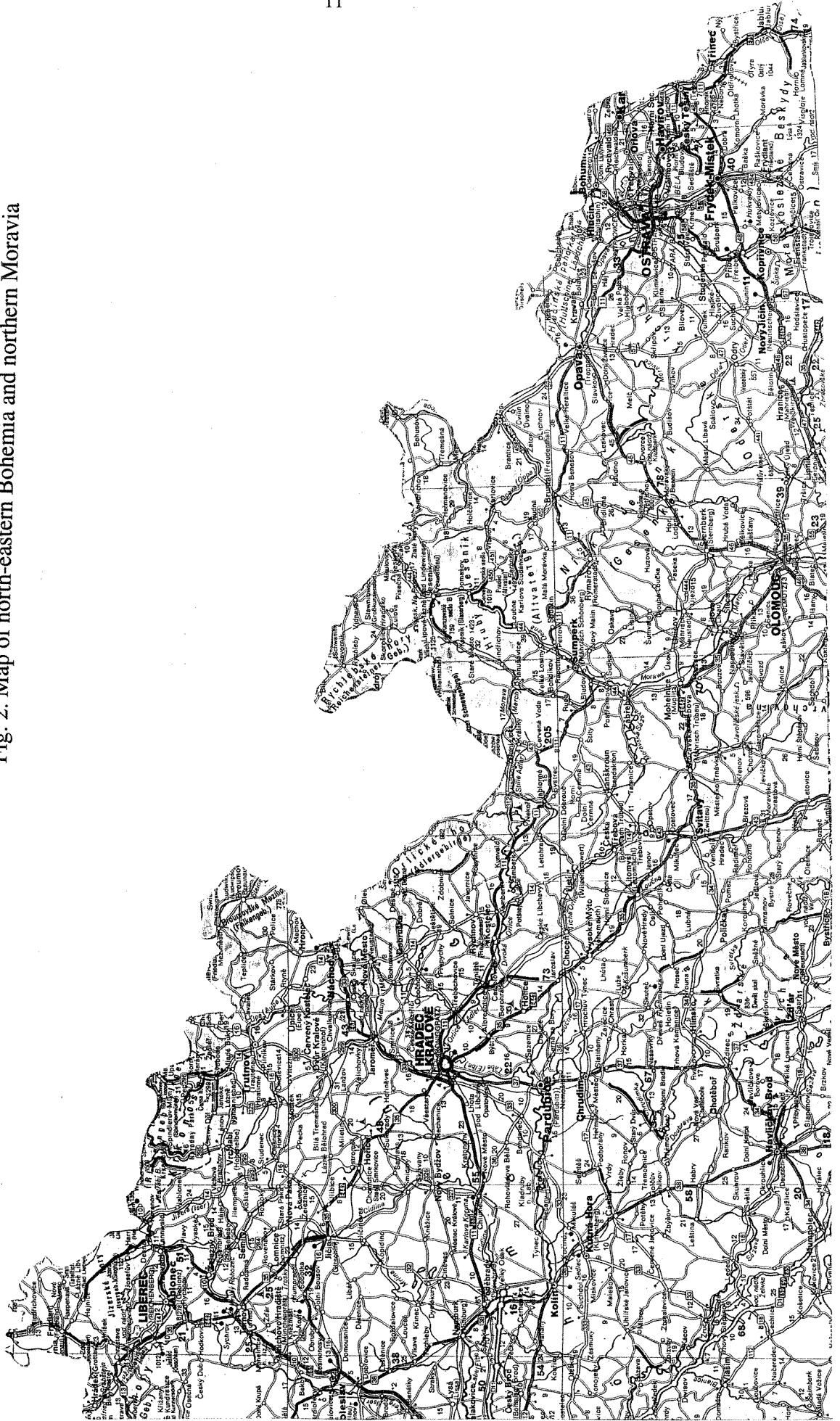
Fig.1. The studied area of The Czech Republic including the EMEP grids (The Co-operative Programme for the Monitoring and Evaluation of the Long-Range Transmission Air Pollutants in Europe).

Most of the eastern part of the sampling area 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. One of the main tributary of River Odra is the River Ostravice which is draining water from northern part of Moravskoslezské Beskydy Mts. Other tributaries of the River Odra have sources in Podbeskydská 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 Hrubý Jeseník Mts. where it originates by confluence of Bílá Opava (White Opava), Střední Opava (Middle Opava) and Černá Opava (Black Opava). The catchment of River Moravice, a tributary of Opava, corresponds to a larger part of Nizký Jeseník Mts. River Opavice, another tributary of Opava start in the western part of Nizký Jeseník Mts. River Osoblaha with a smaller catchment flows in northern direction into Poland. River Bělá from the northern side of Hrubý Jeseník Mts., River Vidnavka, and small water streams from Rychlebské Hory Mts. on the Polish territory join River Kladska Nisa, and form tributaries to the River Odra.

A small part of the studied area belongs to 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 Kralický Sněžník and flows southwards at the western boundary of the studied territory. River Morava has the tributaries Bránná and Desná coming from Hrubý Jeseník Mts. Southern part of Moravskoslezské Beskydy Mts. is drained by the River Běčva, another tributary of the River Morava.

The entire western part of the studied area belongs to the catchment of River Labe (Elbe) which flows into the North Sea. Orlické Hory Mts. are drained by River Orlice and its tributaries Dědina, Bělá and Zdobnice. Broumov Hills form the catchment of River Metuje, and Krkonoše Mts. are drained by Labe itself and its tributary Úpa. The western part of Krkonoše Mts. and eastern part of Jizerské Hory Mts. belong to the catchment of River Jizera which also joins River Labe.

Fig. 2. Map of north-eastern Bohemia and northern Moravia



4.2 Geological composition of the area

The bedrock geology of the studied area is illustrated by geological map in Fig. 3.

The main geological formations in the studied area are:

1. Crystalline of East and West Sudeten.
 - 1.1. Crystalline rocks of Hruby Jesenik Mts.
 - 1.2. Crystalline rocks of Orlicke Hory Mts. - Kladsko (including Rychlebske Hory Mts. and Kralicky Sneznik Group).
 - 1.3. Crystalline rocks of Krkonose Mts. and Jizera Mts.
2. Palaeozoic (Lower Carboniferous) sediments (greywackes, siltstones, shales) of Nizky Jesenik Mts. and Oderske vrchy Hills.
3. Cretaceous and Palaeocene sediments (sandstones, siltstones, shales) of Beskydy Mts., and Podbeskydska pahorkatina Hills - Outer (Flysh) Western Carpathians.
4. Neogene and Quaternary cover of Moravian Gate and Ostrava Basin.
5. Permian sediments (arkoses, sandstones, siltstones) of piedmont area of Krkonose Mts.
6. Cretaceous sediments (sandstones, claystones, marlstones) of piedmont areas of Krkonose Mts. and Orlicke Hory Mts.

4.3 Climatological conditions

Data on precipitation and evaporation used for estimation of runoff, are most important for calculation of critical loads. A map of annual mean precipitation for the period between 1900 and 1950 (Atlas of Climate of the Czechoslovak Republic) was used for evaluation of precipitation (Fig. 4).

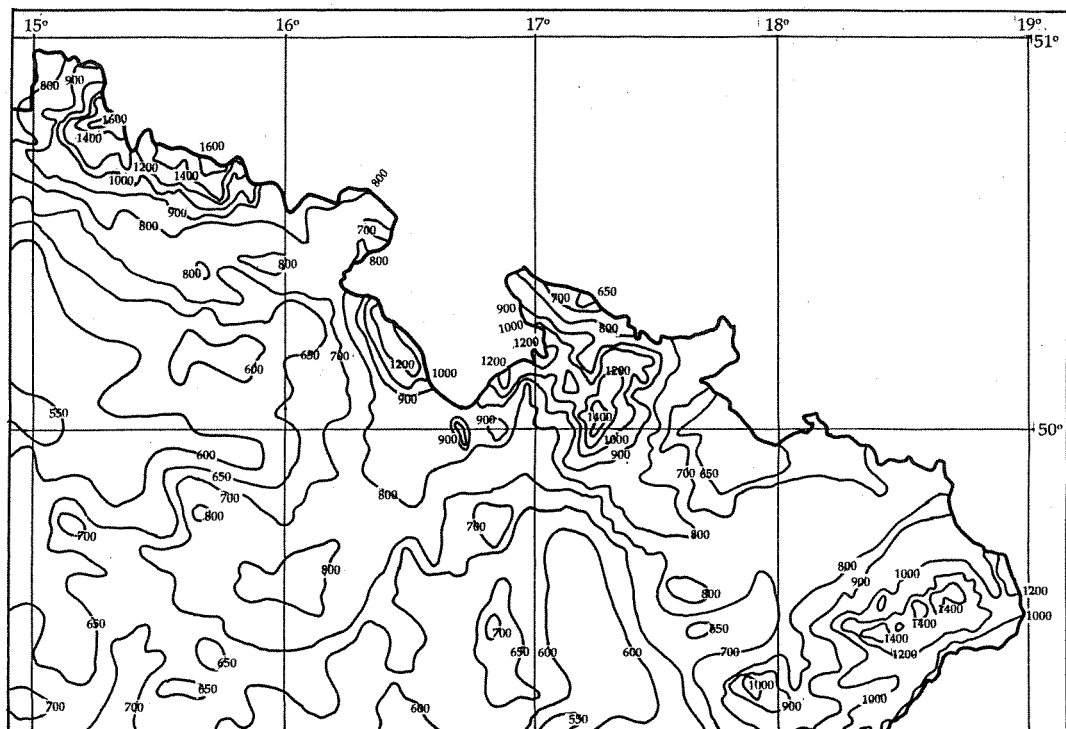


Fig. 4. Annual average precipitation in mm for the period 1900 - 1950.

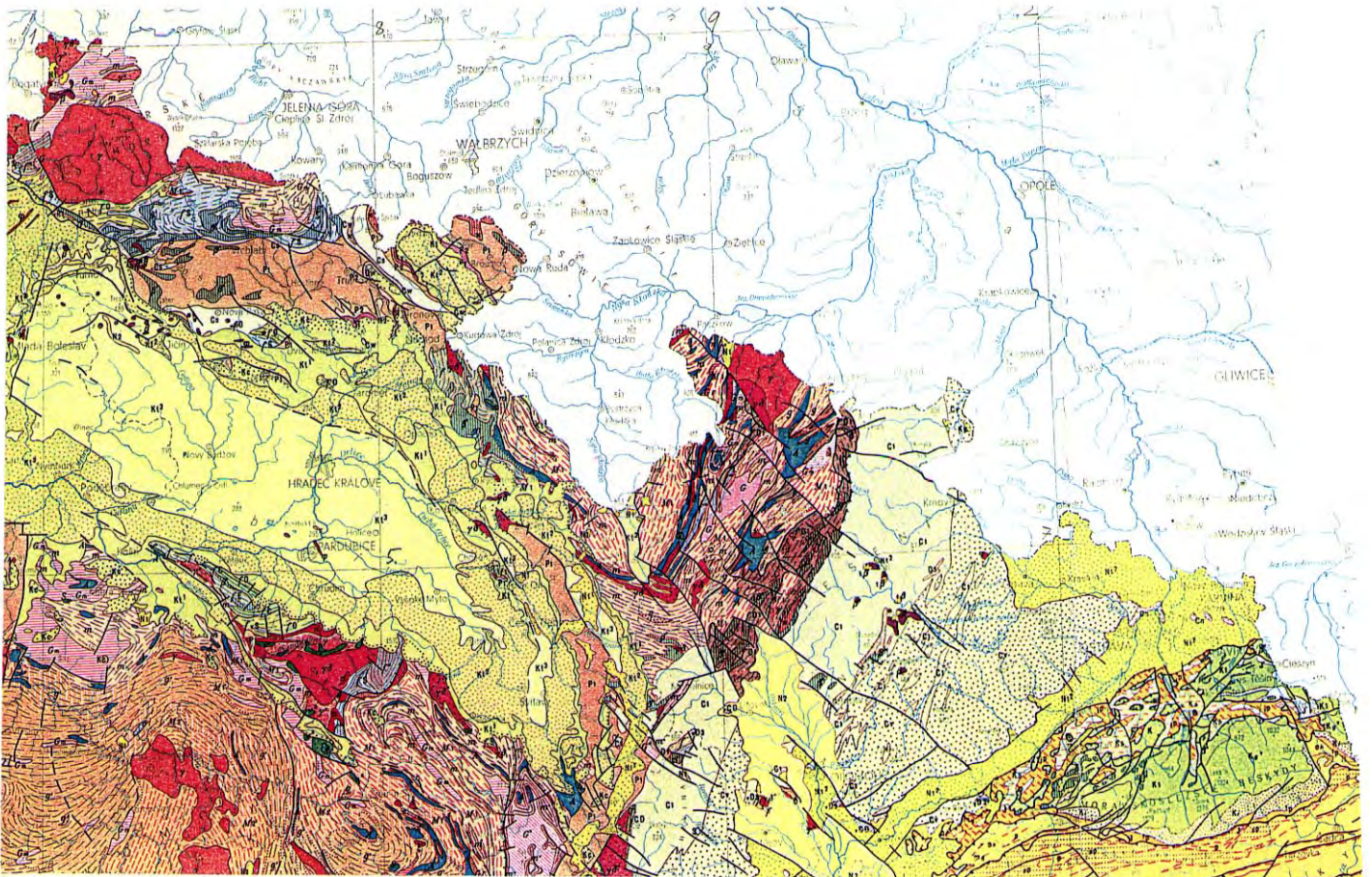


Fig. 3. Geological map of north-east Bohemia and northern Moravia.

Annual mean precipitation reaches values above 1400 mm in Moravskoslezské Beskydy Mts., Hrubý Jeseník Mts., and Krkonoše Mts. The highest values occur in Krkonoše Mts., the north-western part of the studied territory (above 1600 mm). Precipitation increases with altitude above sea level, from the piedmont areas (900 mm at the height of about 300 m a.s.l.) to the top of the mountain ridges (1400 - 1600 mm at altitudes of 1400 - 1600 m a.s.l.).

The studied area 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 north-eastern Moravia, the precipitation maximum is often shifted to the end of summer (August).

Evaporation maps provided by the Czech Hydrometeorological Institute are prepared for open 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.

4.4 Soil

The prevailing soil types of the area of Hrubý Jeseník Mts., Orlické hory Mts., Krkonoše Mts., Jizerské hory 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, podzols 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.

Nizký 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 is frequently covered by 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. Similar types of soils are also found on Cretaceous sediments in eastern Bohemia.

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 Krkonoše Mts., Jizerské hory Mts., Orlické hory Mts., Hrubý Jeseník Mts., and Moravskoslezské Beskydy Mts.

4.5 Vegetation

Forest is the prevailing vegetation in the mountain regions of Krkonose Mts., Jizerske hory Mts., Orlicke hory Mts., Hruby Jesenik Mts., and Moravskoslezske Beskydy. In the region of Nizky Jesenik 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 Krkonose Mts., Jizerske hory Mts., Orlicke hory Mts., Hruby Jesenik 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 Jesenik 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*). The timberline in Krkonose Mts. is located to higher altitude.

Spruce forest dominates also in the Nizky Jesenik 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 cretaceous area of eastern Bohemia Moravian Gate, Ostrava Basin, Opava Upland and most of area of Podbeskydska 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 Moravskoslezske 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. The results from northern Moravia (Raclavsky et al. 1993) showed pronounced variations and larger deviations from long-term averages during spring months. The second half of the 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 September - October confirmed that this month is a suitable period for sampling (Lien et al. 1994).

5.2 Sampling

The water samples were collected between 6th and 27th October 1993 and between 12th and 17th September 1994. 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 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 other areas it was necessary to sample every suitable stream. Due to 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. 5.

Additional data from western part of the Czech Republic are taken from (Aanes et al. 1995) and from unpublished data (Jiri Kopacek pers. comm.).

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, conductivity, calcium, magnesium, sodium, potassium, sulphate, and values for chloride, alkalinity, nitrate, ammonium, total organic carbon (TOC), reactive aluminium (RAI), and labile aluminium (LAI).

For a number of samples there was a considerable difference between sums of cations and anions in 1993. A maximum of 30 % difference was accepted. The differences between sum of cations and anions were all less than 10 % in 1994.

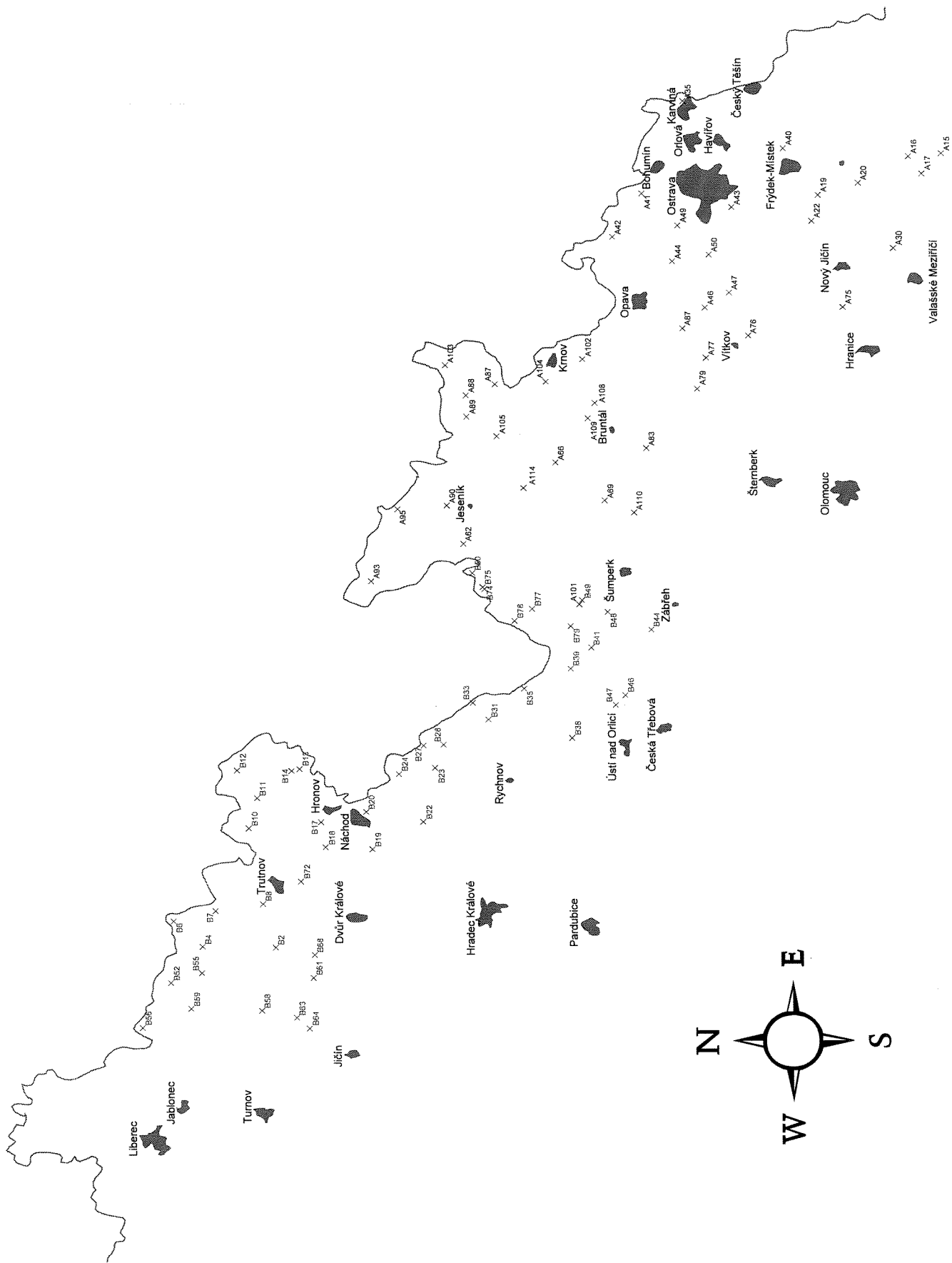


Fig. 5 Sampling sites in north-eastern Bohemia and northern Moravia.

In order to identify systematic reasons for the differences in 1993, 12 water samples from the Czech laboratory were also analysed at NIVA. The parallel analyses showed good or quite good correlations for calcium, 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 (Lien et al 1994).

It was therefore decided to perform analyses from all sampling localities both at TUO and at NIVA in 1994. The 81 parallel analyses showed with few exceptions good correlations for all parameters analysed: pH, alkalinity, conductivity, nitrate, sulphate, chloride, calcium, magnesium, sodium, and potassium. The parallel analyses are presented in appendix 3.

The chemical values used for calculations of critical load and exceedance of critical load were analysed at TUO for the samples A15 - A114, and at NIVA for the samples B2 - B79 and C104 - C114. The samples D131 - D135 were analysed elsewhere (Appendix 3).

6. CRITICAL LOADS OF NORTH-EASTERN BOHEMIA AND NORTHERN MORAVIA

Values of critical loads of acidity CL and values of their exceedances CL_{ex} were calculated according to the formula described in Chapter 3. ANC_{limit} was set to 20 ueq/l. Runoff was calculated from the annual average of precipitation minus 30 % reduction for evaporation. The sulphur deposition value for EMEP grids in the Czech Republic was prepared by the Czech Hydrometeorological Institute, Prague, after recalculation (Table 1). The deposition values for base cations were used in the calculation according to the International Institute for Applied System Analysis (IIASA), following recommendations of International Co-ordination Centre for Effects (Hetteling et al. 1991). The EMEP grids are presented in Fig. 1.

Table 1. Sulphur and base cation depositions for the various EMEP grids examined in the Czech Republic (Czech Hydrometeorological Institute).

EMEP grid	Sulphur deposition keq/km ² /year	Base cation deposition keq/km ² /year
23 - 16	115	29
23 - 17	318	32
24 - 16	86	43
24 - 18	295	35
25 - 18	254	42

By comparing the total annual deposition of oxidised sulphur on the Czech Republic territory between the period of 1985 - 1989 with 1992 and 1993 (Tuovinen et al. 1994), the reduction of sulphur is close to 30 %. A 30 % reduction of the sulphur deposition given by the Czech Hydrometeorological Institute was used for the calculation of exceedance of critical loads.

Table 2 contains the values of critical loads for all grids arranged according their numbers (Fig. 6). The centre of each grid is specified by geographical co-ordinates (latitude and longitude) in degrees. The values of precipitation for each grid are given together with the number of water samples representing the grid. From these columns we can also identify water samples used for several grids that do not have their own representative sample. When one representative sample is used for the calculation of critical load in an adjacent grid, the results may differ if there is a difference in precipitation. One column contains a simplified code for the geology in the 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 show values of critical loads and exceedances.

Compared to the study of critical load and exceedance of critical load in northern Moravia and Silesia (Lien et al. 1994), the calculations in the present study is more conservative: The base cations are calculated without any adjustments for transport of sea salt, the depositions of sulphur are reduced with 30 % according to the reduced values of sulphur deposition in this part of Europe, and the calculation of exceedance of critical load is not taking into account any acidifying effect of nitrate.

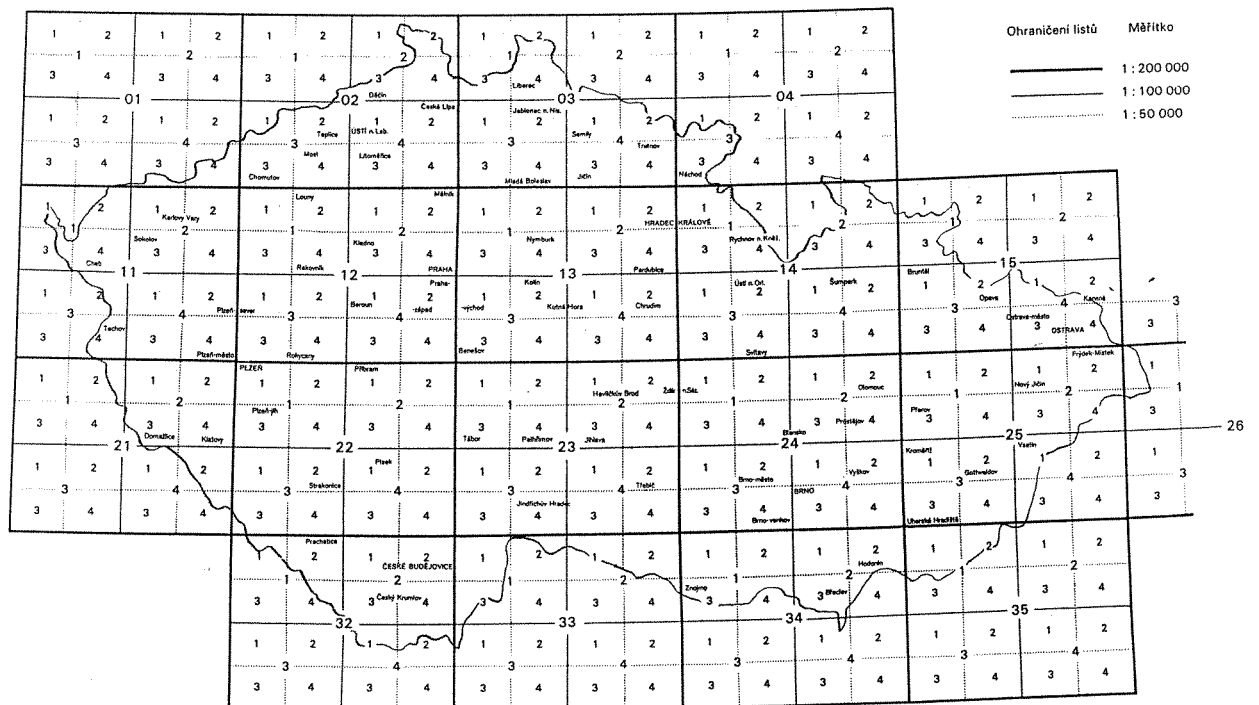


Fig. 6. Numbers of sampling grids using the numbering system of topographical maps.

Table 2. The grid number (Fig. 6), 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	LATITUDE	LONGITUDE	PRECIP.	GEOL.	SAMPLE	CL	CL _{EX}
2.313	50.59742	13.39865	660	1	C113	64	158
3.142	50.86028	15.23931	1320	1	C114	176	30
3.144	50.77486	15.23972	1000	1	C114	123	83
3.231	50.86059	15.40686	1310	1	B56	129	77
3.233	50.77517	15.40724	1100	1	B56	103	104
3.234	50.77525	15.57476	1390	1	B52	131	76
3.243	50.77509	15.74227	1490	1	B6	101	105
3.411	50.68975	15.40762	830	1	B59	145	62
3.412	50.68983	15.57510	900	1	B55	85	121
3.413	50.60441	15.40838	750	5	B63	1391	-1185
3.414	50.60441	15.57545	780	1	B58	43	163
3.421	50.68967	15.74258	980	1	B4	126	81
3.422	50.68927	15.91006	870	1	B7	909	-702
3.423	50.60425	15.74289	770	5	B2	1897	-1691
3.424	50.60385	15.91033	800	5	B8	1308	-1101
3.431	50.51890	15.40838	690	5	B64	979	-773
3.432	50.51898	15.57579	740	5	B61	1648	-1442
3.441	50.51882	15.74320	720	5	B68	146	61
3.442	50.51842	15.91061	750	5	B72	1876	-1670
3.444	50.43300	15.91089	665	5	B19	2487	-2280
4.311	50.68948	16.07752	820	6	B10	653	-447
4.312	50.69028	16.24499	780	5	B12	248	-41
4.313	50.60406	16.07777	790	6	B10	628	-422
4.314	50.60487	16.24520	780	6	B11	297	-91
4.321	50.69086	16.41246	750	5	B12	237	-30
4.323	50.60544	16.41264	740	5	B12	233	-27
4.331	50.51863	16.07801	740	5	B17	617	-410
4.332	50.51945	16.24541	790	6	B14	464	-258
4.333	50.43321	16.07826	660	5	B18	952	-746
4.334	50.43402	16.24562	840	5	B20	1286	-1079
4.341	50.52002	16.41281	850	5	B13	648	-442
4.434	50.43491	16.91510	890	1	A93	435	-257
4.443	50.43454	17.08246	720	1	A93	344	-166
11.144	50.08250	12.56738	650	1	C107	139	-58
11.233	50.08328	12.73459	700	1	C104	74	6
11.411	49.99785	12.73553	800	1	C104	89	-9
14.111	50.34778	16.07850	630	6	B22	3127	-2920
14.112	50.34860	16.24583	810	1	B24	378	-172
14.113	50.26236	16.07875	665	6	B22	3302	-3096
14.114	50.26318	16.24605	720	1	B23	139	68
14.121	50.34918	16.41317	1050	1	B27	325	-119
14.123	50.26376	16.41335	1010	1	B28	207	0
14.124	50.26410	16.58065	1020	1	B33	226	-20
14.141	50.17833	16.41353	850	1	B31	167	40

GRID	LATITUDE	LONGITUDE	PRECIP.	GEOL.	SAMPLE	CL	CL _{EX}
14.142	50.17868	16.58080	890	1	B35	131	47
14.143	50.09290	16.41371	840	5	B38	207	-29
14.144	50.09325	16.58095	850	1	B39	175	3
14.212	50.34950	16.91518	1120	1	B50	351	-173
14.214	50.26407	16.91526	1100	1	B50	344	-166
14.221	50.34912	17.08251	1010	1	B50	313	-135
14.222	50.34852	17.24983	840	1	A95	2463	-2286
14.223	50.26370	17.08256	1110	1	A62	1723	-1545
14.224	50.26310	17.24985	1050	1	A90	1204	-1026
14.231	50.17878	16.74807	920	1	B78	176	1
14.232	50.17865	16.91534	880	1	B75	183	-5
14.233	50.09336	16.74819	930	1	B79	208	-30
14.234	50.09323	16.91543	790	1	B77	164	13
14.241	50.17828	17.08261	1020	1	B74	415	-238
14.242	50.17768	17.24987	1230	1	B74	509	-332
14.243	50.09286	17.08266	870	1	B77	185	-7
14.244	50.09225	17.24989	1200	1	A114	405	-227
14.321	50.00747	16.41389	830	5	B47	1102	-924
14.322	50.00782	16.58110	810	6	B46	1477	-1300
14.411	50.00793	16.74831	770	1	B41	193	-16
14.412	50.00780	16.91551	740	1	B49	392	-214
14.413	49.92250	16.74842	690	1	B44	431	-253
14.414	49.92237	16.91560	685	1	B48	961	-784
14.421	50.00743	17.08272	850	1	B49	456	-279
14.422	50.00682	17.24991	890	1-2	A69	664	-486
14.424	49.92140	17.24994	760	2-1	A110	751	-573
15.113	50.26310	17.41714	960	2-1	A89	592	-414
15.114	50.26371	17.58442	760	2	A88	885	-707
15.123	50.26409	17.75171	720	2	A103	1361	-1184
15.131	50.17768	17.41712	880	2-1	A105	839	-661
15.132	50.17829	17.58438	710	2	A87	900	-722
15.133	50.09226	17.41711	830	2-1	A66	1109	-931
15.134	50.09287	17.58434	640	2	A104	1037	-859
15.141	50.17867	17.75164	710	2	A87	900	-722
15.143	50.09325	17.75157	630	2	A104	1020	-843
15.311	50.00683	17.41710	790	2	A109	989	-811
15.312	50.00745	17.58430	690	2	A108	1016	-838
15.313	49.92140	17.41710	810	2	A83	1110	-932
15.314	49.92202	17.58426	720	2	A79	1351	-1174
15.321	50.00783	17.75150	660	2	A102	1255	-1077
15.322	50.00797	17.91869	640	4	A42	1107	-930
15.323	49.92241	17.75143	650	2	A78	1174	-996
15.324	49.92255	17.91859	710	4	A42	1233	-1055
15.332	49.83660	17.58422	790	2	A79	1487	-1309
15.341	49.83698	17.75136	740	2	A77	1437	-1259
15.342	49.83712	17.91849	730	2	A46	786	-608
15.343	49.75155	17.75129	750	2	A76	1365	-1187
15.344	49.75170	17.91840	720	2	A47	834	-657

GRID	LATITUDE	LONGITUDE	PRECIP.	GEOL.	SAMPLE	CL	CL _{EX}
15.411	50.00788	18.08588	660	4	A42	1143	-965
15.413	49.92246	18.08576	710	4-2	A44	597	-419
15.414	49.92213	18.25292	710	4	A41	1203	-1025
15.423	49.92156	18.42007	730	4	A35	1135	-957
15.424	49.92075	18.58722	760	4	A35	1183	-1005
15.431	49.83703	18.08563	720	2	A49	692	-514
15.432	49.83670	18.25276	730	4	A43	1967	-1789
15.433	49.75161	18.08550	770	4	A50	799	-622
15.434	49.75128	18.25260	800	4	A50	832	-654
15.441	49.83613	18.41988	750	4	A35	1167	-989
15.442	49.83533	18.58700	780	4	A35	1216	-1038
21.442	49.14442	13.24515	1200	1	D131	35	25
22.331	49.14507	13.41198	1100	1	D133	37	23
22.333	49.05965	13.41274	1220	1	D134	13	47
25.122	49.66627	17.91830	710	4-2	A75	1856	-1678
25.124	49.58084	17.91820	700	3-4	A75	1829	-1651
25.211	49.66618	18.08537	800	3	A22	2170	-1993
25.212	49.66585	18.25244	910	3	A19	2764	-2586
25.213	49.58075	18.08525	910	3	A30	1227	-1049
25.214	49.58042	18.25229	1200	3	A20	479	-301
25.221	49.66528	18.41951	940	3	A40	1778	-1600
25.231	49.49532	18.08512	890	3	A30	1199	-1021
25.232	49.49499	18.25214	1100	3	A17	514	-336
25.241	49.49442	18.41914	1250	3	A16	625	-448
25.243	49.40899	18.41896	1230	3	A15	628	-451
32.142	48.80646	13.91511	950	1	D135	10	51

Basic statistical parameters of critical values for the set of 118 grids samples are summarised below (units keq/km²/year):

	Critical loads	Exceedances
Average mean	810	- 629
Median	650	- 450
St. deviation	690	684
Minimum value	10	-3096
Maximum value	3302	163

7.2 MAPS OF CRITICAL LOAD AND EXCEEDANCE

In many parts of the study area there were very limited possibilities of obtaining samples which were not contaminated by local sources of pollution like agriculture (fertilising, livestock) or other human activities. 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.

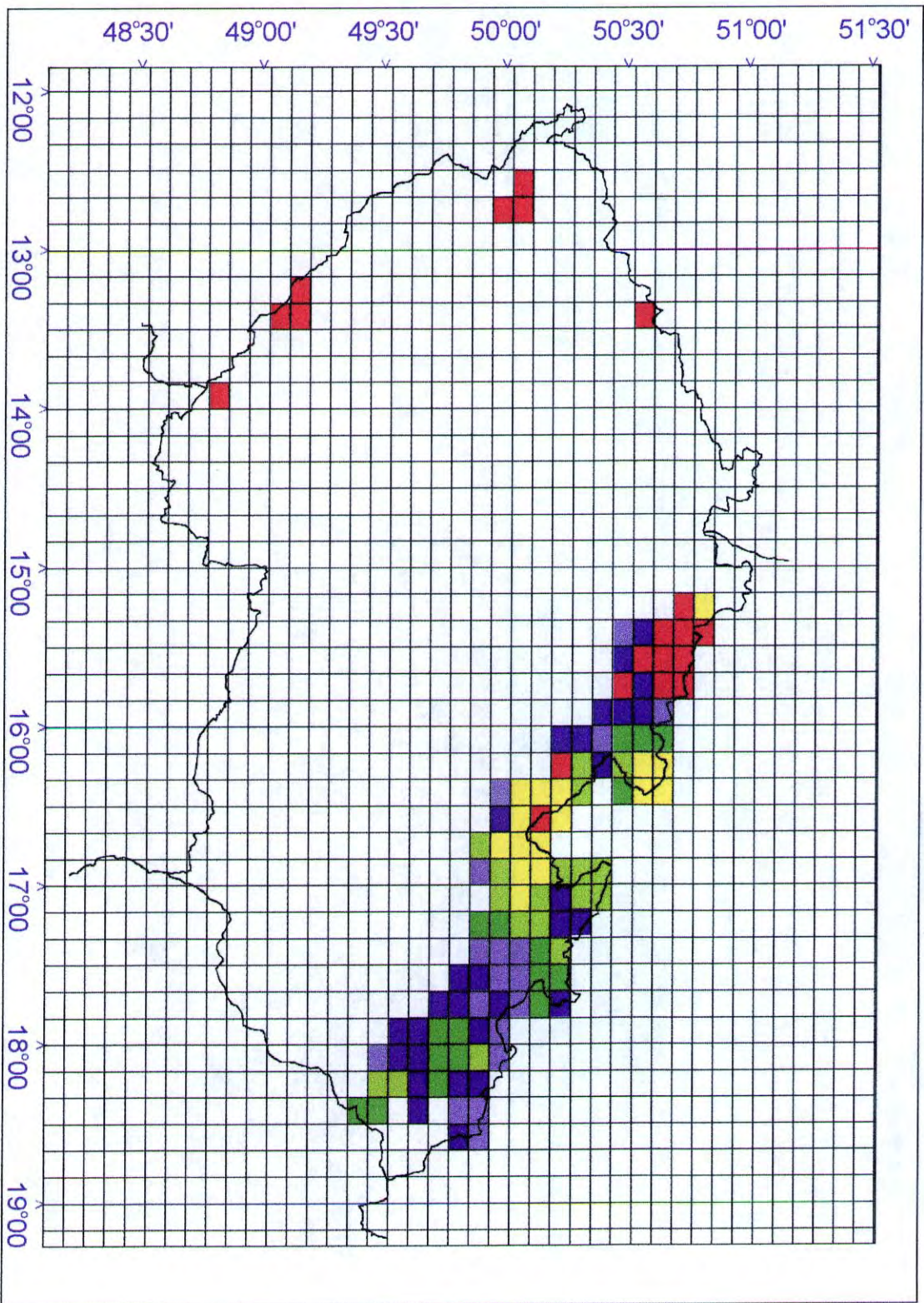
The grid size for the construction of critical load maps should be adjusted to the density of available sampling localities and also to the division of map sheets. Practical reasons have led to the selection of grids which correspond to one quarter of a map sheet in scale 1:50 000. Each grid had a size 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. The grids are numbered using the system of map numbering. The numbers of the individual grid units are shown in the map Fig. 6, and the 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 in 1993 and 10 % in 1994. 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 the selected samples is illustrated by crosses and sample numbers in the map of the sampling sites (Fig. 5).

Fig. 7 shows critical loads of acidity (CL) for the individual grids. The critical load values are expressed in keq/km²/year and as g S/m²/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 high acid deposition. In parts of north-eastern Bohemia the critical load values are much lower.

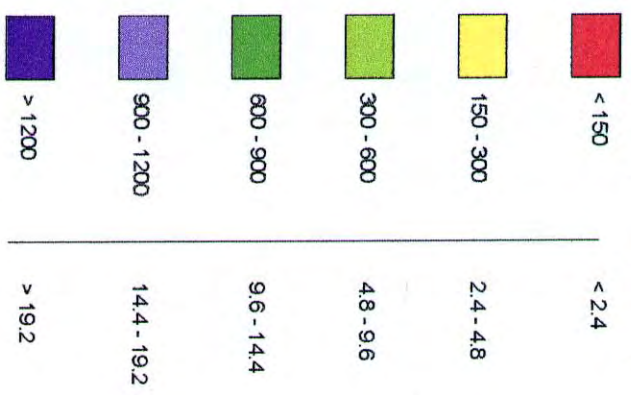
From the total number of 118 grids (Fig. 9), there are 20 grids (approximately 17% of the area) in the lowest class 0 - 150 keq/km²/year. A critical load value of zero was found only for one sample, but this sample was not evaluated to be representative for any of the grids. In each of the four groups, (150-300), (300-600), (600-900), and (900-1200) keq/km²/year there are between 16 and 18 grids (13 - 15 % of the study area). 25 % of the studied area had a critical load of more than 1200 keq/km²/year.

The distribution of values of critical loads for the different groups are illustrated in Fig. 9. For the values of exceedances a similar graph is presented in Fig. 10. The groups correspond to the values and colours in the maps. A wide range and dispersion are seen for values of both the critical loads and their exceedances.



CL

keq.km².yr⁻¹ g.S.m².yr⁻¹



Equidistant Cylindrical Projection



Fig. 7. Map of critical load of acidity to surface waters in north-eastern Bohemia northern Moravia.

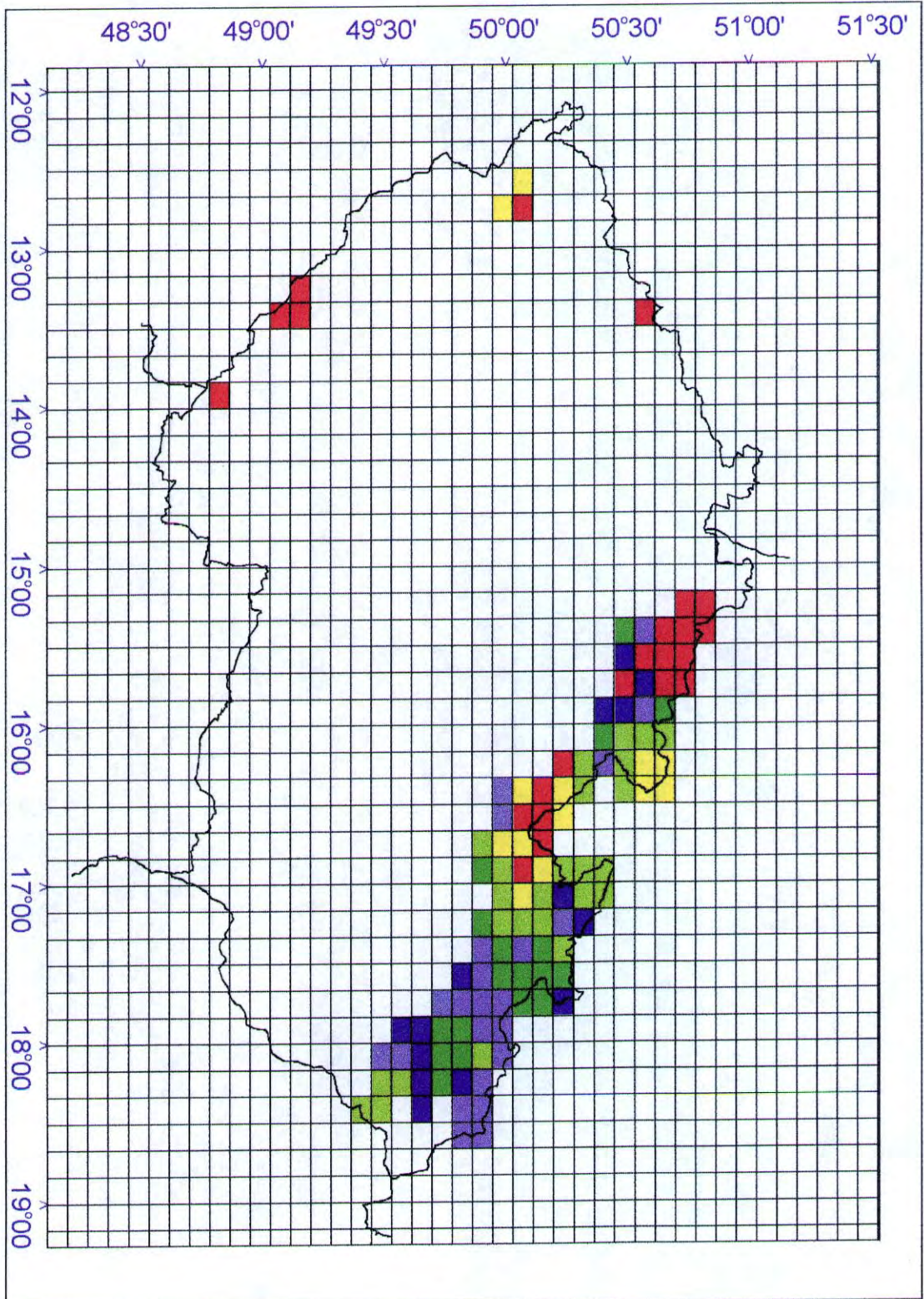


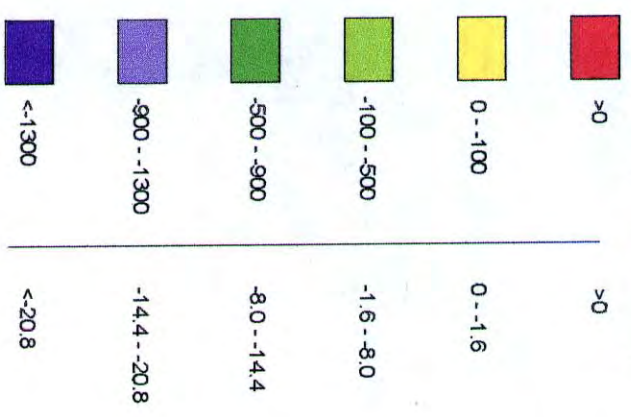
Fig. 8. Map of exceedance of critical load of acidity to surface waters in north-eastern Bohemia and northern Moravia.



CLEX

keq.km².yr⁻¹

g.S.m².yr⁻¹



Equidistant Cylindrical Projection



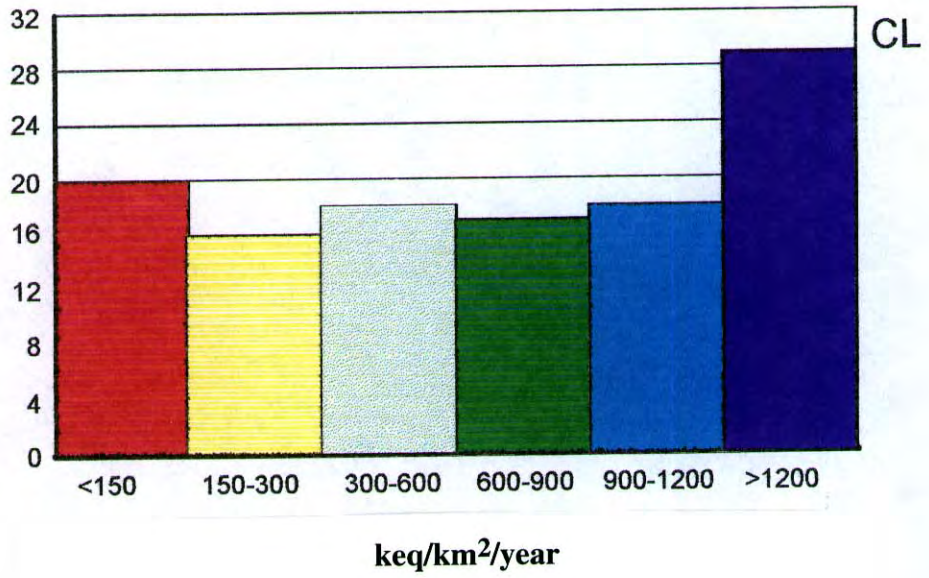


Fig. 9. Frequency distribution of critical load values.

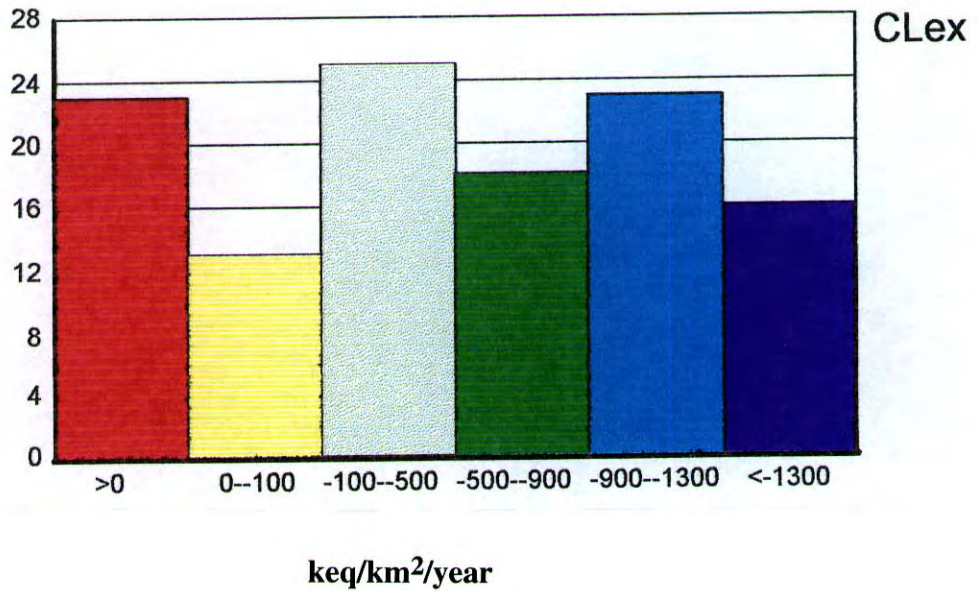


Fig. 10. Frequency distribution of exceedance values of critical loads.

Fig. 8 presents the map of exceedance of critical loads of acidity. The units are $\text{keq}/\text{km}^2/\text{year}$. The group of high degree of danger (exceedance values above 0 $\text{keq}/\text{km}^2/\text{year}$, red coloured) are mainly located to the Jizerske Hory Mts., Krkonose Mts. and Orlicke Hory Mts. In addition, scattered water analysis from western and south-western Bohemia showed exceedances of critical loads. Another category close to exceedance (between 0 and - 100 $\text{keq}/\text{km}^2/\text{year}$, yellow coloured) are found in Broumovske mezihoi Hills, Orlicke Hory Mts. and Jesenik Mts.

Approximately 13 400 km^2 , or 17 % of the total area of The Czech Republic, have been examined for critical load and exceedance (Table 3). 2.500 km^2 or 19 % showed exceedance of critical load (Fig. 9, red colour) and an other area of 1.500 km^2 (11 %) are near to exceedance (Fig. 9, yellow colour). Parts of these area was probably exceeded few years ago when the deposition of sulphur was higher. Due to the present conservative calculations of critical load and exceedance (page 19) some parts of this area might still be exceeded.

Table 3. Groups of exceedance of critical load, the number of examined grids, percentage of total grids, and area of each group of exceedance.

CL_{EX} group $\text{keq}/\text{km}^2/\text{year}$	Number of grids	% of grids	Total area km^2
>0	22	19	2.500
0 -- 100	13	11	1.500
-100 -- 500	24	20	2.700
-500 -- 900	19	16	2.200
-900 -- 1300	21	18	2.400
< -1300	19	16	2.200

8. CONCLUSIONS

Approximately 13 400 km^2 , or 17 % of the total area of The Czech Republic, have been examined for critical load and exceedance. 2.500 km^2 or 19 % of the examined area showed exceedance of critical load, and an other 1.500 km^2 (11 %) was near to exceedance. Parts of this area were probably exceeded some years ago when the deposition of sulphur was higher.

Calculations of critical loads and exceedance of critical loads in various scattered areas of western and south-western Bohemia showed low values. Further studies of critical load in the Czech Republic should therefore be continued in these regions.

Inter-comparison of water analyses between Technical University, Ostrava and Norwegian Institute for Water Research showed with a few exceptions, good agreement.

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APPENDIX 1. METHODS OF CHEMICAL ANALYSIS OF WATER SAMPLES AT TUO.

** 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 in 0.5 litre PVC bottles and conserved with 5 ml conc. HCl per litre.

C. For all other analyses 1.5 litre 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". All analyses were done in the laboratory of the Department of Geology, Mineralogy and Geochemistry at the Technical University in Ostrava (M. Adamusova, Head of the Laboratory).

** pH*

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

** Conductivity*

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

** 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 $0.6 \mu\text{m}$ the water was evaporated under 105°C and weight of the remnant was determined. The amount of dissolved matter is given as mg/l . The values are not included in the table Appendix 2.

** Particulate matter*

Non-dissolved matter (NP) was determined together with dissolved matter by gravimetric method. The membrane filter, Synpor, of $0.6 \mu\text{m}$ 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 . The values are not included in the table Appendix 2.

*** 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: bromocresol 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 Zeiss, 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 ug/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 isotachopheresis at an isotachopheretic 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 AT TUO.

Results of the chemical analyses of water samples: pH, electrical conductivity, Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁺, Cl⁻, alkalinity, NO₃⁻, NH₄⁺, TOC, Al_r, and Al_{ijl}.

YEAR	DATE	No	pH	COND	CA	MG	NA	K	SULF	CL	ALK	NO3	NH4	TOC	RAL	LAL
1993	6-27Okt	A15	7.13	12	13.03	3.04	1.3	2	12.52	2.7	820	970			563	442
1993	6-27Okt	A16	7.2	11	14.03	3.04	0.4	1.3	12.95	2.7	720	1900			111	74
1993	6-27Okt	A17	7.16	11	15.03	1.22	0.4	0.8	10.37	2.7	720	1540			46	26
1993	6-27Okt	A19	6.65	47	83.17	9.12	0.5	1.7	28.8	7.1	4470	5030			5	4.7
1993	6-27Okt	A20	7.16	13	15.03	0.61	1.1	1.7	16	3.5	570	140			9	7.8
1993	6-27Okt	A22	6.81	52	68.14	7.3	17	70	125.9	16	2520	610			7	6.1
1993	6-27Okt	A30	6.85	29	31.06	9.12	12	3.4	45.64	6.2	2470	2760			1	1
1993	6-27Okt	A35	7.07	45	64.13	9.73	9	3.7	106.7	23	2920	1570			237	191
1993	6-27Okt	A40	7.24	33	46.09	11.6	9	9	54.8	22	2000	310			446	275
1993	6-27Okt	A41	7.06	32	35	7.9	13	8	33.4	37	520	9140			9	6
1993	6-27Okt	A42	7.1	20	23	19.5	8	7	35.8	9.8	1270	540			951	675
1993	6-27Okt	A43	6.91	52	48.1	17	22	11	54.8	36	3670	5420			49	37
1993	6-27Okt	A44	7.03	23	22	9.73	7	7	54.2	9.8	270	1060			18	13
1993	6-27Okt	A46	7.18	25	26.05	9.73	6	8	47	6.2	1630	190			65	50
1993	6-27Okt	A47	6.99	28	35.07	9.12	7	7	61.44	11	1520	900			92	31
1993	6-27Okt	A49	7.06	31	28.6	15.8	7	8	87.13	15	620	2890			6	4
1993	6-27Okt	A50	6.55	32	37.07	10.3	10	8	87.13	12	420	4900			83	48
1993	6-27Okt	A62	7.74	16	24.05	12.8	5.4	6.4	19.7	2.7	1420	2160			286	110
1993	6-27Okt	A66	7.62	15	21.04	10.3	5.6	6.4	17.24	2.7	1220	1460			22	16.4
1993	6-27Okt	A69	7.44	8	12	6.69	5.1	6.4	20.77	0.9	670	1970			102	60
1993	6-27Okt	A75	7.44	37	60.12	7.9	11	6.6	24.93	3.5	3370	4130			59	24
1993	6-27Okt	A76	6.89	29	38.08	17.6	8.7	6.4	59.9	12	920	4900			620	425
1993	6-27Okt	A77	7.25	41	45.09	19.5	12	9	85	27	670	9310			491	180
1993	6-27Okt	A78	7.37	30	28.06	20.7	12	7.3	56	27	1220	3730			12	5
1993	6-27Okt	A79	7.74	29	37.07	17	9.5	9.2	56	8.9	1970	740			307	106
1993	6-27Okt	A83	7.74	15	19	12.8	7.6	6.4	23.67	7.3	1270	860			669	272
1993	6-27Okt	A87	7.18	27	22	20.7	9.1	7.9	73.65	9.8	1070	2100			108	40
1993	6-27Okt	A88	7.65	28	11	18.9	11	8	50.86	9.8	2020	1060			562	171
1993	6-27Okt	A89	7.15	18	17	9.12	7.5	0	48.68	6.2	420	530			304	112
1993	6-27Okt	A90	7.26	17	28	6.69	5.3	0	24.8	7.1	1120	2850			240	175
1993	6-27Okt	A93	6.97	15	12	10.3	7.9	0	50.86	6.2	420	480			332	45
1993	6-27Okt	A95	7.62	39	69.14	14.6	9	7.9	49	15	2670	1670			329	133
1993	6-27Okt	A102	7.7	33	38	12.8	17	12	58.14	16	2220	2030			142	62
1993	6-27Okt	A103	6.7	35	48.1	12.8	14	6.4	70.39	21	1170	6980			72	7
1993	6-27Okt	A104	7.77	32	44.1	14	13	6.3	81.69	12	2020	1800			101	70
1993	6-27Okt	A105	7.78	11	21	5.47	7.2	5.8	27	5.3	620	1960			150	76
1993	6-27Okt	A108	7.81	20	24	12.8	10	6.4	33.68	5.3	1170	2050			165	87
1993	6-27Okt	A109	7.22	18	23	12.2	9.5	6.3	42.75	7.1	820	1680			178	53
1993	6-27Okt	A110	7.7	9	14	6.7	7.5	6	13	5.3	870	1870			241	49
1993	6-27Okt	A114	7.26	8.77	10	1.52	2.6	1.2	16	0.8	520	1910			10	0
1994	12-19Sep	B2	8.13	41.7	59	11.1	15	1.2	47	10	3335	2130	7	2.1	12	2
1994	12-19Sep	B4	6.14	4.21	3.69	0.78	1.2	0.9	12.9	0.9	16	375	5	1.3	53	20
1994	12-19Sep	B7	7.71	17.9	27.7	4.79	1.2	0.7	15.9	1.7	1432	1270	5	1.2	30	20
1994	12-19Sep	B8	7.71	33.9	49.9	10.8	3.8	1	58	5	2077	2140	7	0.77	16	6

YEAR	DATE	No	pH	COND	CA	MG	NA	K	SULF	CL	ALK	NO3	NH4	TOC	RAL	LAL
1994	12-19Sep	B10	7.42	21.7	38.5	1.09	1.4	1.3	45.2	3.2	973	1810	5	1.5	77	33
1994	12-19Sep	B11	7.03	19.8	26.8	3.57	3.1	1.9	59.6	4.4	296	1790	5	4	10	0
1994	12-19Sep	B12	7.1	14.5	13	3.79	4.3	4.4	37.2	3.2	243	1780	5	1.7	10	0
1994	12-19Sep	B13	7.71	17.3	26.7	2.15	1.7	1.8	24.8	3.6	813	3580	5	0.89	10	0
1994	12-19Sep	B14	7.46	16.8	23.6	3.15	1.4	2.5	33.2	3.2	569	3360	5	3.2	79	29
1994	12-19Sep	B17	7.77	24.2	25	12.1	1.9	2.3	55.6	4	1079	1390	8	2.1	10	0
1994	12-19Sep	B18	7.68	34.5	57	4.71	4.2	1.6	65	11	1261	6660	8	3.2	20	10
1994	12-19Sep	B19	8.09	67.2	115	13.1	9.8	2.8	93	24	4622	3760	8	3.2	10	0
1994	12-19Sep	B20	7.89	33.5	55	6.23	5.3	0.9	62.5	5	1916	2370	5	2.5	10	0
1994	12-19Sep	B22	7.99	78.1	156	14.6	4.5	2.5	102	14	6279	3710	13	3.6	10	-5
1994	12-19Sep	B23	6.79	10.8	10.4	2.91	3	1.5	31.6	2.4	111	1710	7	1.2	12	2
1994	12-19Sep	B24	7.34	14.1	19.2	2.78	2.7	1.3	30.8	2.4	484	1890	11	5.9	23	13
1994	12-19Sep	B27	6.94	7.52	8.25	1.65	1.3	1.3	12	4.4	156	1820	5	0.38	10	0
1994	12-19Sep	B28	6.02	5.16	5.38	0.62	1.8	1.2	9.9	1.2	106	1300	5	1.3	64	19
1994	12-19Sep	B31	6.62	5.86	5.64	1.3	2	0.9	15.9	1.2	85	705	5	5.1	137	30
1994	12-19Sep	B33	6.88	5.82	5.49	1.61	1.9	0.9	14.2	1.1	147	445	5	3.8	38	27
1994	12-19Sep	B35	4.68	8.59	6.53	1.4	2.5	1.3	26	2.8	0	580	5	6.5	700	478
1994	12-19Sep	B38	6.73	19.7	22.3	5.42	4.9	1	67.6	3.2	225	615	6	4.2	30	20
1994	12-19Sep	B39	6.65	9.22	8.54	1.89	3.6	1.1	26.4	2.4	55	1920	5	1.5	35	15
1994	12-19Sep	B41	6.65	8.91	8.01	2.06	3.6	0.9	21.2	1.6	82	3030	5	1.4	30	17
1994	12-19Sep	B44	7.7	21.5	23.7	6.13	8	2.4	55.2	3.6	792	990	5	2.7	10	0
1994	12-19Sep	B46	7.86	35.5	61	8.41	5.1	1.5	65	3.5	2238	1095	26	8.2	14	4
1994	12-19Sep	B47	7.73	29.7	48.9	3.64	8.9	1	58.5	9	1352	1870	5	5.2	10	0
1994	12-19Sep	B48	8	25.7	17.5	20.5	6.7	1.1	39.2	4.4	1745	830	6	2.8	10	0
1994	12-19Sep	B49	7.66	15.3	16.9	5.04	4.1	0.7	31.2	2	731	995	5	2.3	10	0
1994	12-19Sep	B50	7.23	7.85	8.08	1.83	2.6	0.9	14.2	1.1	247	1960	5	1.1	14	4
1994	12-19Sep	B52	4.84	4.06	2.24	0.47	1.5	0.5	10.3	0.9	0	675	5	2.3	491	330
1994	12-19Sep	B55	6.18	3.08	2.63	0.74	0.9	0.3	7.7	0.7	21	640	5	1.8	91	17
1994	12-19Sep	B56	4.66	4.73	2.46	0.64	1.6	0.4	12.8	0.7	0	370	7	4.8	556	405
1994	12-19Sep	B58	5.4	14.3	15.5	2.97	3.2	0.4	50.8	3.2	36	15	26	4.8	292	211
1994	12-19Sep	B59	6.62	5.09	4.84	1.25	1.5	0.4	12.9	1.5	73	475	5	1	29	10
1994	12-19Sep	B61	7.99	35.7	49.8	15.2	4.4	2.3	37	6	2852	1380	5	2.8	10	0
1994	12-19Sep	B63	7.99	30.5	46	10.8	5.5	0.7	36.5	4	2339	1145	5	1.9	10	0
1994	12-19Sep	B64	7.42	31	34	13.4	7.4	1.1	52	12	816	9700	5	1.5	10	0
1994	12-19Sep	B68	5.11	11.9	12	2.49	2.7	1.6	31.6	6.4	19	2110	5	3.3	146	94
1994	12-19Sep	B72	7.83	44.5	72.6	14.6	4.2	1.3	69	11	2943	1075	5	1.7	10	0
1994	12-19Sep	B74	7.43	10.8	12.7	2.86	3.1	0.9	20.1	1.3	415	2050	5	0.79	10	0
1994	12-19Sep	B75	6.61	6.13	6.02	0.98	2.4	0.8	13.8	1	61	1800	5	1.9	195	29
1994	12-19Sep	B77	6.51	9.02	9.65	1.47	3	0.6	25.2	1.3	57	2120	5	1.09	17	7
1994	12-19Sep	B78	6.43	5.95	5.42	1.1	2.5	0.7	15.2	1.2	43	1680	5	1.2	34	21
1994	12-19Sep	B79	6.55	8.18	6.67	1.18	5.3	0.8	22	2	60	1420	5	2.5	67	22
1993	11-Nov	C104	3.97	9.07	4.1	0.76	2.6	0.9	23	1.5		185		16.5	1440	980
1993	11-Nov	C107	5.43	8.47	7.5	2.03	4	1.2	25.5	2.4	21	805		8.2	442	164
1993	11-Nov	C113	5.2	14.7	13.8	4.01	3.7	1.5	50	2.8	0	1225		2	393	332
1993	11-Nov	C114	4.67	6.46	4.54	1.05	2.2	0.4	21.2	1.3	0	970		3.2	1488	1308
1993	25Okt	D131	4.78	3.19	0.77	0.44	0.8	0.4	5.8	0.8		936		1.08	604	
1993	25Okt	D133	5.8	1.93	0.77	0.37	1.2	0.2	2.23	0.8	21	654		3.47	147	
1993	25Okt	D134	4.76	2.52	0.5	0.27	0.7	0.4	3.73	0.7		595		3.95	354	
1993	25Okt	D135	4.78	3.41	0.91	0.13	1.1	0.4	8.57	0.7		373		2.38	757	

APPENDIX 3. INTER-COMPARISON OF CHEMICAL ANALYSES BETWEEN NIVA AND TUO.

In 1993, 12 water samples from the critical load studies of The Czech Republic including one blank control, were re-analysed at NIVA. The comparison showed excellent correlation for calcium, and quite good agreements for sodium, sulphate, and with a few exceptions also for nitrate. Chloride was systematically higher in the Czech analysis at TUO while magnesium showed both higher and lower values (Lien et al. 1994).

In 1994 all 81 water samples were analysed both at NIVA and at TUO for pH, alkalinity, conductivity, nitrate, sulphate, chloride, calcium, magnesium, sodium, and potassium. The methods of water analyses used at NIVA are described below. The regression lines and correlation coefficients for all parameters are also shown together with a dotted 1/1 line for each figure. The results of the different parallel analyses are commented for each parameter.

pH

NIVA determines pH by a potentiometric measurement using pH-meter equipped with a combined glass electrode and calomel reference electrode, according to the Norwegian Standard, NS 4720. The Instrument used was Orion Research 901 Ion Analyzer.

Determination of pH has been done at very different times at the two laboratories. Technical University in Ostrava (TUO) determined pH shortly after sampling, while Norwegian Institute for Water Research (NIVA) performed the measurements several weeks later. Storage effects are probably the main reason for the great spread of points in the correlation plot.

Alkalinity

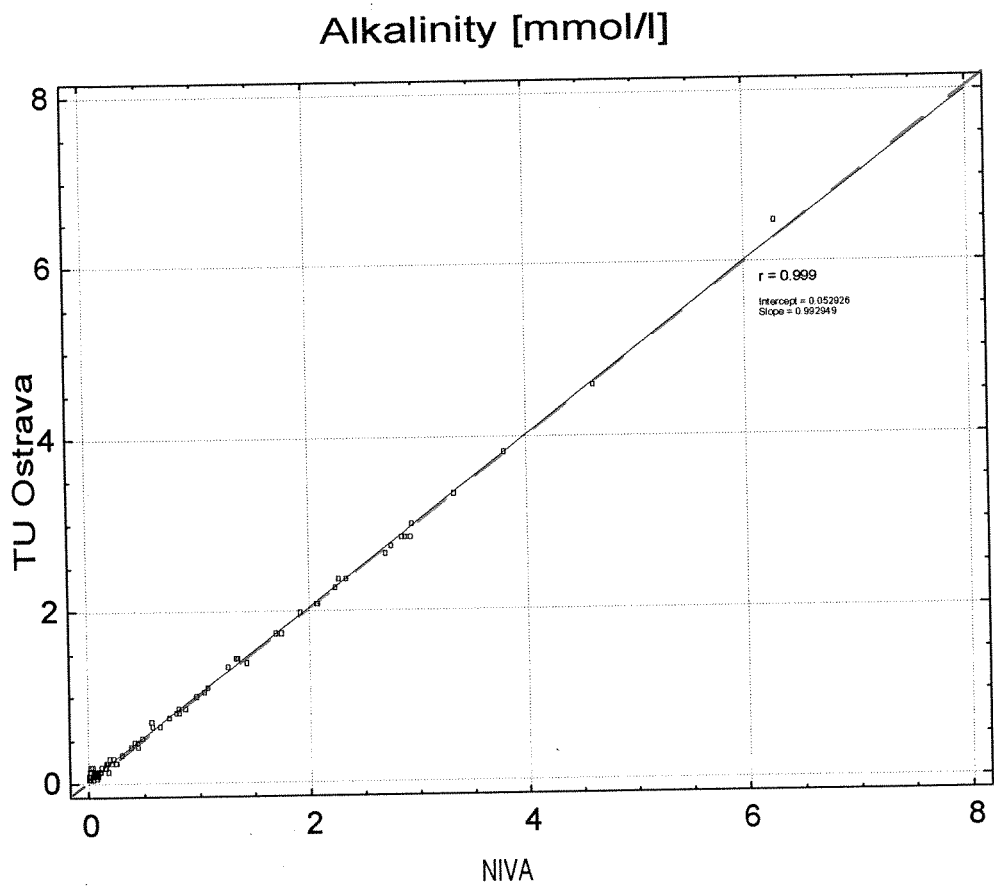
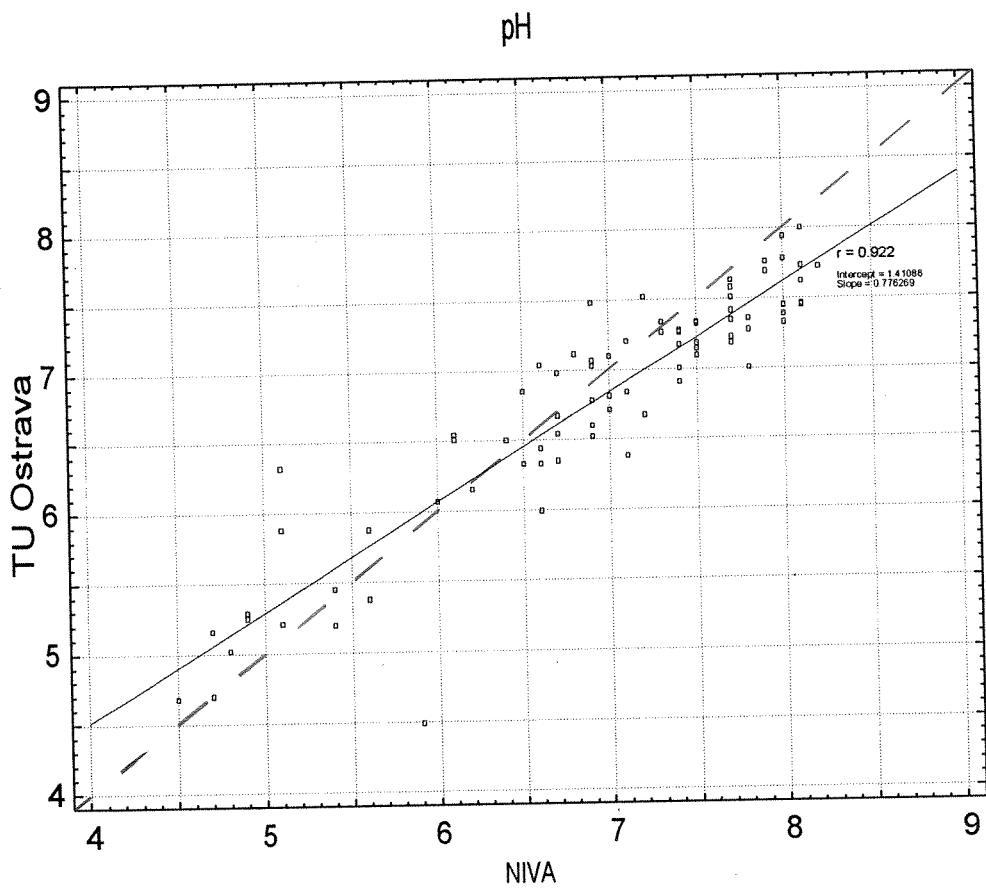
Alkalinity is determined at NIVA by potentiometric titration with hydrochloric acid to pH = 8.3 (phenolphthalein-alkalinity) and to pH 4.5 (total-alkalinity), according to the Norwegian Standard NS 4754. The instrument used was a WTW Microprocessor Conductivity Meter LF 539.

The alkalinity plot shows an excellent correlation between the results of the two laboratories, and with very low random deviations.

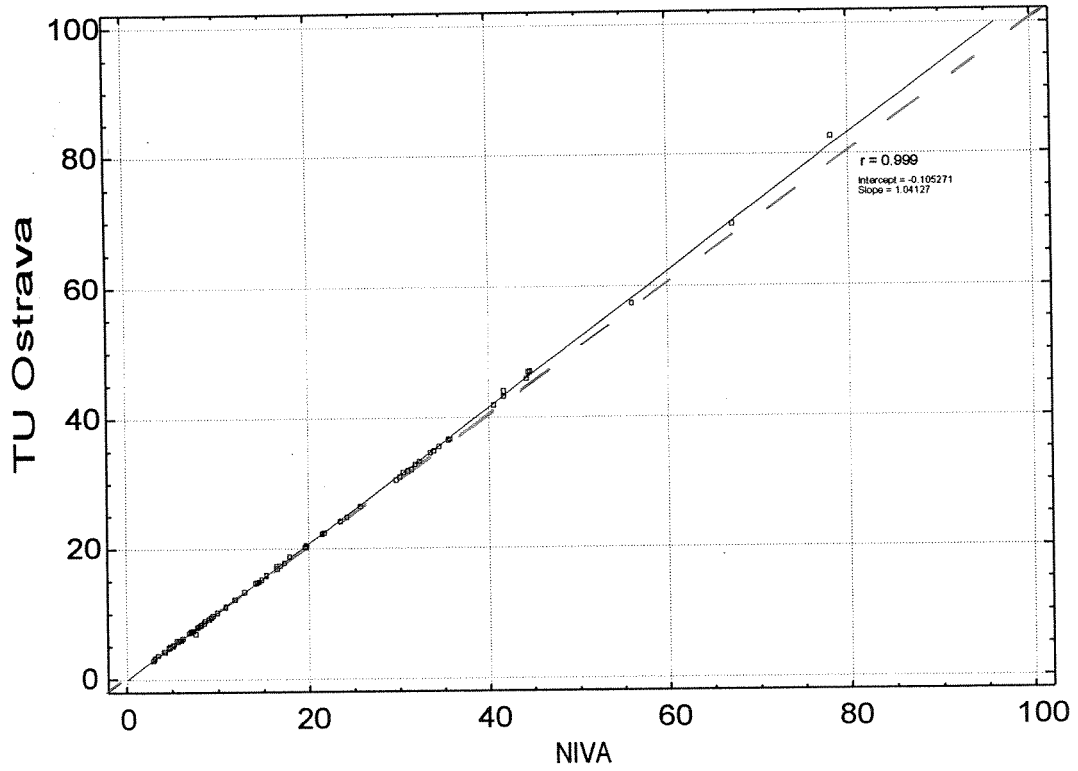
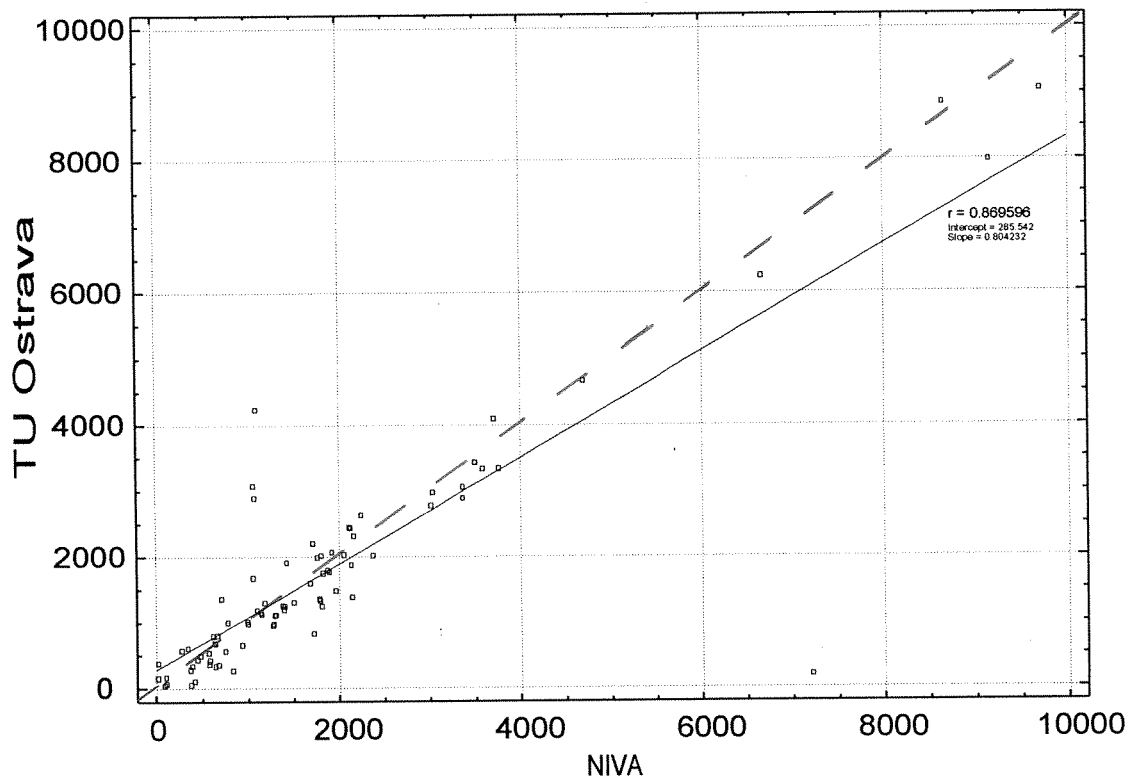
Conductivity

Conductivity is measured at NIVA by an electrometric method following the ISO Standard 7888, using a Philips Conductometer PW 9527 equipped with automatic temperature correction.

The conductivity plot shows excellent correlation between the results of the two laboratories, although the results of TUO are slightly (4 %) systematically higher than those of NIVA. An accurate temperature correction is absolutely necessary to obtain comparable results, as the conductivity is changing 2 % per degree at room temperature.



Conductivity [mS/m]

NO₃ - N [$\mu\text{g/l}$]

Nitrate + nitrite

NIVA used a method based on the reduction of nitrate to nitrite by copperized cadmium in presence of ammonia which buffers the solution, and complexes the cadmium ions formed. Nitrite reacts in strongly acid solution (pH = 1.5 - 2.0) with sulphanilamide to a diazo compound, which is coupled to N-(1-naphthyl)-ethylenediamine to an azo dye. The absorbance is measured at the wavelength 545 nm. The determination is performed with a Skalar autoanalyzer. The method is based on the Norwegian Standard 4745. The detection limit of this method is 1 µg/l.

For this variable the plot shows that the results of the laboratories are influenced by rather great random variations. Exclusion of the one extreme value (NIVA ca. 6500, TUO ca 200) will improve the correlation factor.

TUO used a manual, photometric method which is quite different from the method NIVA used. It is not clear whether or not the nitrite content is determined together with the nitrate by the Czech Standard. Different methods may cause deviations between results, and usually the manual methods show greater spread in the results than the automated method. However, particulate matter will influence the results in both methods if the samples are not filtered before the determination.

Sulphate

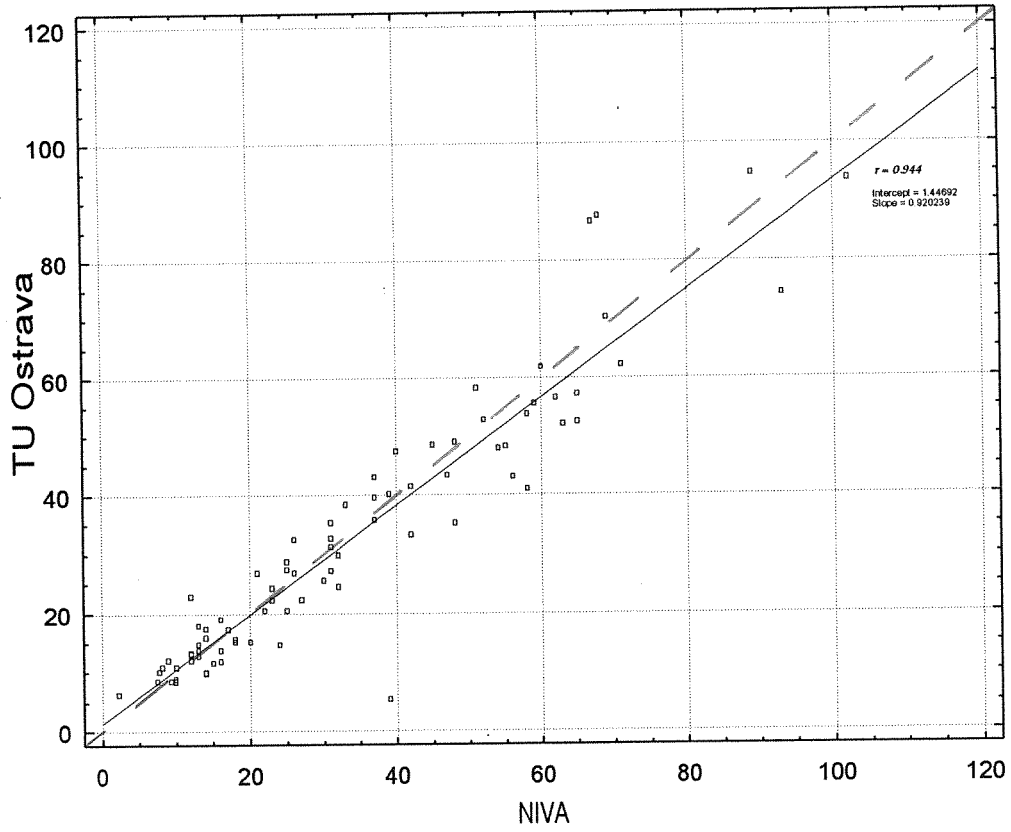
NIVA is using ion chromatography for the determination of sulphate and chloride, and this method is based on the ISO guide 10304-1. The instrument used was a Waters ILC-1 Ion Chromatograph. The detection limit was 0.2 mg/l.

There is a fairly good correlation between the results of the two laboratories, even if the picture is dominated by some random deviations. The methods used at the two laboratories are quite different, but this fact does not seem to have any great influence on the comparability.

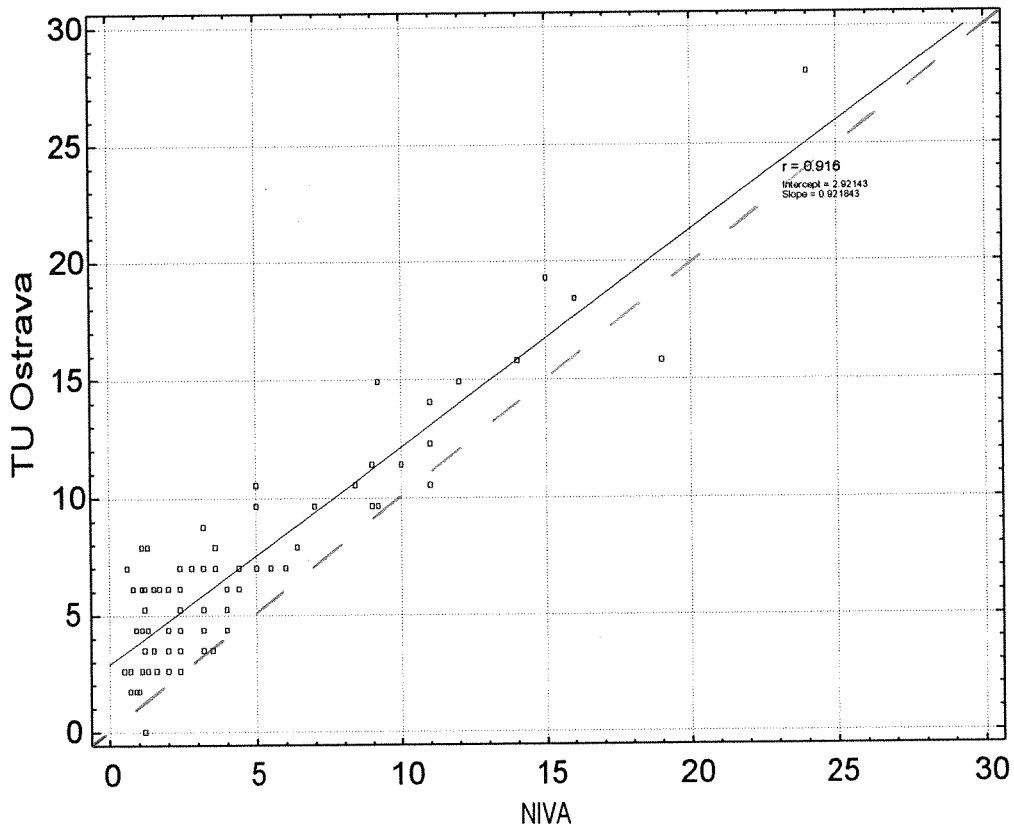
Chloride

The plot is clearly indicating that there is a systematic difference between the result of the two laboratories, with an approximate constant deviation of 2 - 3 mg/l, TUO having the highest values. The methods used at the two laboratories are principally quite different, as NIVA used ion chromatography (detection limit 0.2 mg/l) and TUO used argentometric titration (detection limit about 2 mg/l ?). The deviations between the results of the two laboratories are obvious caused by the differences between the two methods used.

SO₄ [mg/l]



Cl [mg/l]



Calcium

NIVA used an ICP technique, while TUO used chelatometric titration. There is a good correlation between TUO and NIVA for this variable, however, NIVA has systematically higher results (less than 10 %) compared to TUO. The reason for this is probably due to the fact that two quite different methods have been used at the two laboratories.

Magnesium

NIVA used an ICP technique, while TUO determined magnesium by an indirect method: firstly the sum of calcium and magnesium is determined by chelatometric titration, then calcium alone is determined by the same technique, and magnesium is calculated as the difference between these two determinations.

For this variable too there is a fairly good correlation between the results of TUO and NIVA. However, there is a constant deviation between the results of approximately 0.5 - 0.6 mg/l, and this is most certainly caused by the fact that the laboratories used principally different methods.

Sodium

For sodium the correlation factor is good, but the results from TUO are systematically lower (roughly 10 %) than those from NIVA. TUO used flame photometry and NIVA used ICP for the determination of sodium, and this is probably the main reason for the observed deviations.

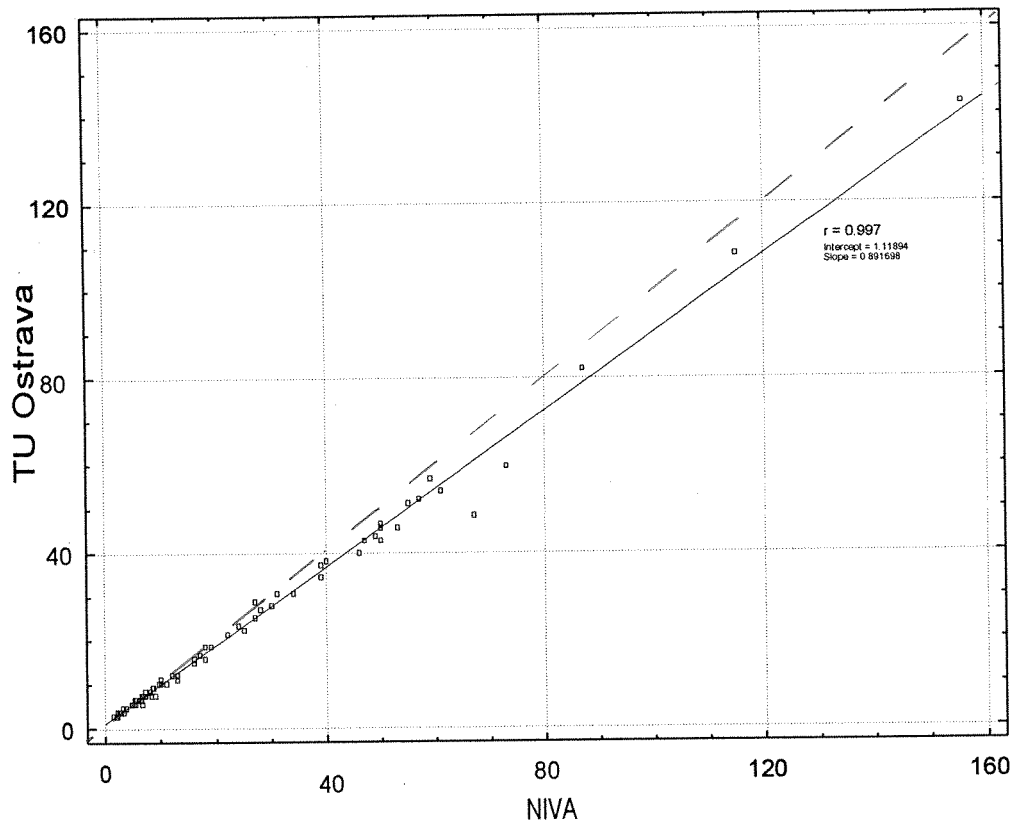
Potassium

There is a systematic deviation in the results from NIVA and TUO, The TUO results being roughly 8 % higher than from NIVA. TUO determined potassium by flame photometry, while NIVA used flame atomic absorption spectrometry. By earlier test of these two techniques we found that the flame emission method routinely gave about 8 % higher results than atomic absorption.

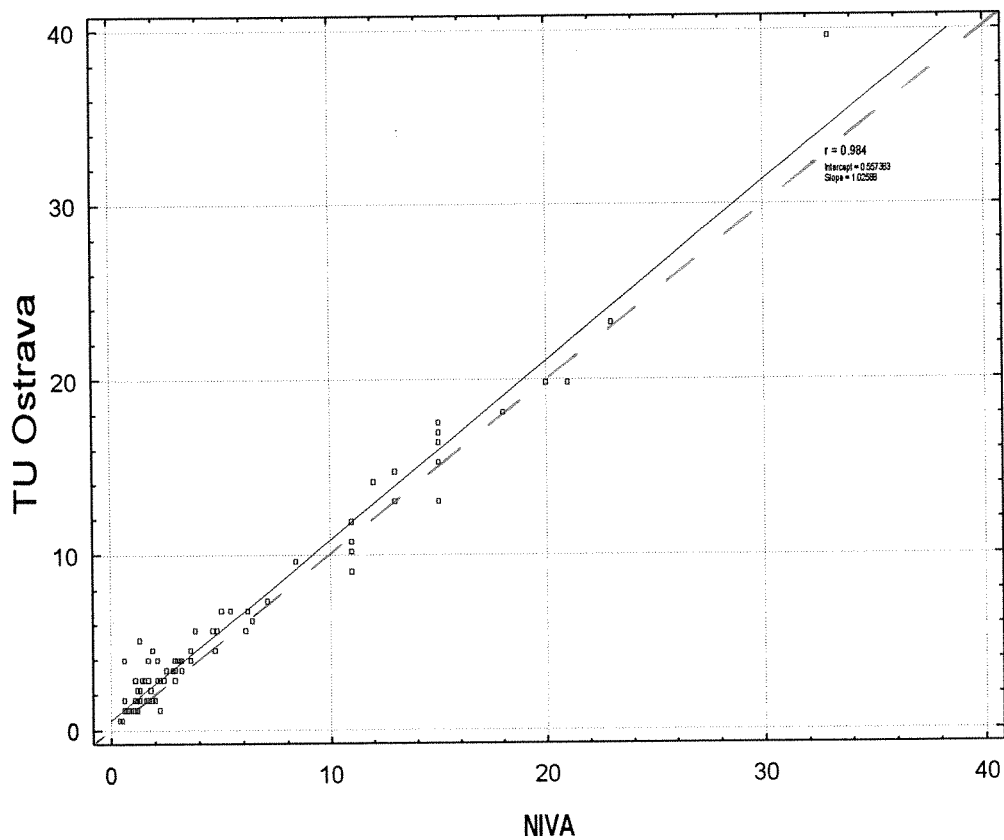
In general.

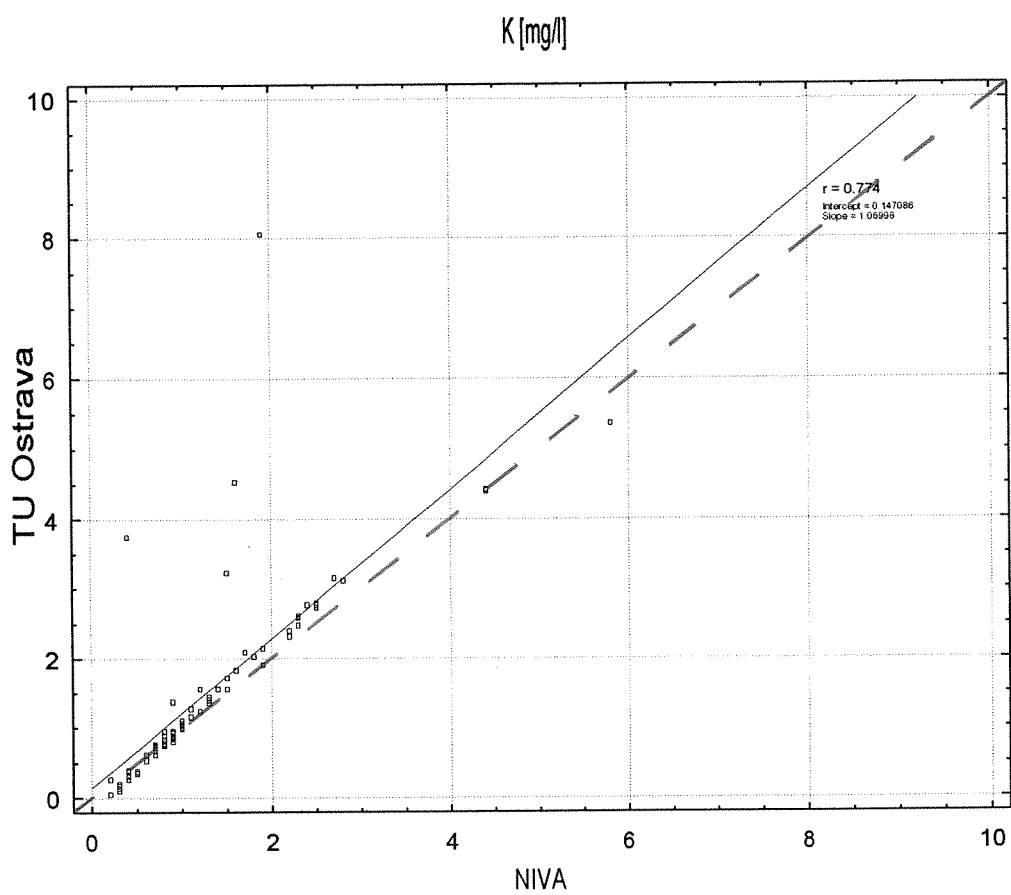
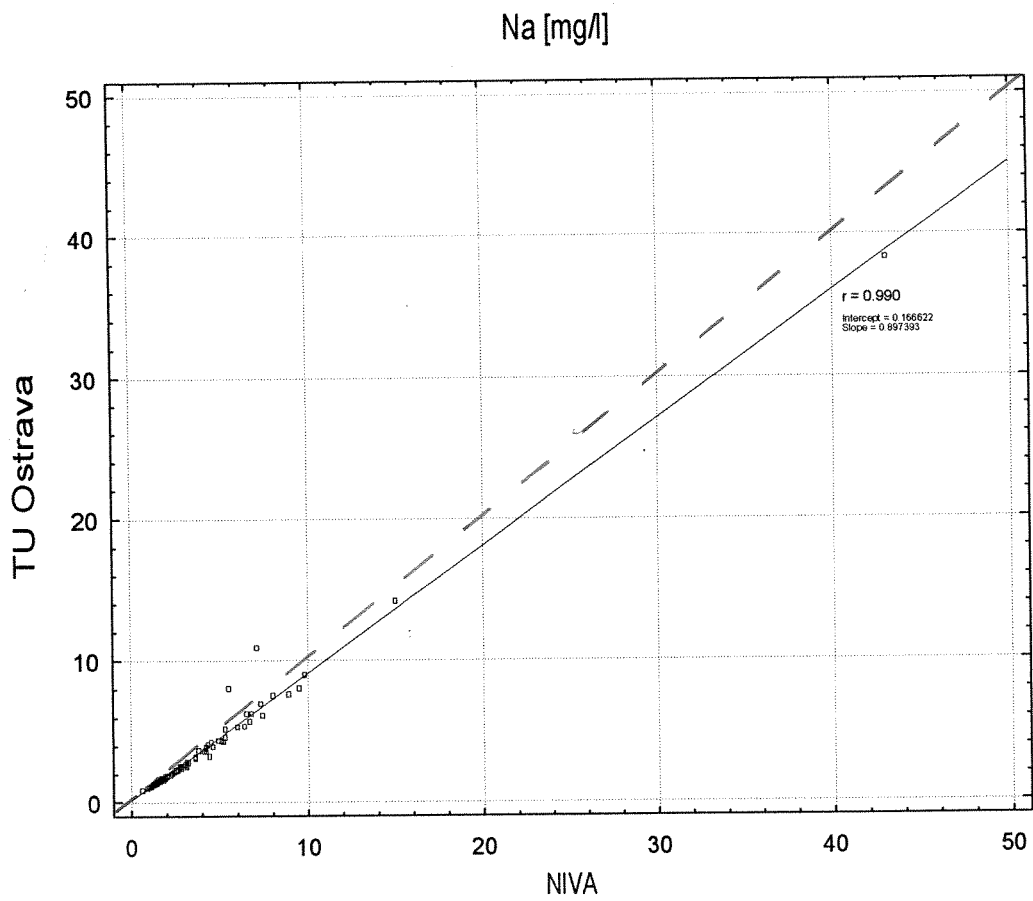
Compared with the 12 parallel analyses for six parameters performed between the two institutes in 1993, the 1994 results showed improvements for magnesium, sodium, and sulphate. However, chloride is still systematically 2-3 mg/l higher at NIVA compared to TUO, as it was in 1993. For calcium and nitrate there were no big difference between the two years.

Ca [mg/l]



Mg [mg/l]





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