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Impact of Diffuse Nitrate Pollution Sources on Groundwater Quality—Some Examples from Czechoslovakia

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In several regions of Czechoslovakia with intensive agricultural production, the correlation between the amount of nitrogen fertilizer applied and the nitrate content in groundwater has been recognized. Nitrate pollution of groundwater is considered to be the most serious source of nonpoint pollution in Czechoslovakia.

A program of research into the effects of farming activities on groundwater quality in Czechoslovakia is under way on experimental fields (20 to 30 hectares) and, simultaneously, in regions in which shallow, vulnerable aquifers occur. The importance of the soil organic matter's stability for maintaining the groundwater quality is emphasized. Research based on nitrogen and organic carbon balance has shown that the restoration of a soil-groundwater system is a complicated process that usually requires changes in the extent and intensity of agricultural activities and consistent attention to the effects produced by natural conditions. Regional investigation of the impact of farming on shallow aquifers in the fluvial deposits of the Elbe River in Bohemia has proved the hydrochemical instability and vertical hydrochemical heterogeneity of these aquifers.

The WASTEN deterministic model was used for modeling the transport and transformation of various types of inorganic fertilizers. The input data is based on laboratory and field measurements. Special topics are the verification of model calculations and the time and spatial variability of input data with respect to the unsaturated zone. The research results are being used for making regional and national agro-groundwater managerial schemes more precise, as well as for decision-making.

Introduction

Czechoslovakia, a landlocked Central European country (population of 16.2 million, area of 127,871 square km), is located on the European watershed of the Northern, Baltic, and Black Seas. The country's geographical position, its continental type of precipitation, high density of population (126 per km^2), and intensive industrial and agricultural production all underline the importance of water as the top-priority natural resource for man's life and the nation's economic development. As early as the Middle Ages, the great seasonal fluctuations of water resources and their irregular distribution over the state territory led to the construction of large water-management projects. In the 15th century, an extensive system of ponds and basins was established in Southern Bohemia to control the surface runoff, reduce the frequency of floods and lessen the extent of wetlands. From the very beginning, about 4300 ponds have been used for intensive fisheries. The fishpond system, without any substantial changes, has remained in operation up to our times.

Other evidence of the water resources' significance for Bohemia is the age-old tradition of climatological and hydrological measurements as a basis for the study of the origin and quantity of water resources. Regular and reliable observations of precipitation at the Klementinum station in Prague have been carried out since 1804, while air temperature measurements have been made since as early as 1775. The surface runoff in the Labe River, at the site where it leaves the state territory (the town of Děčín), has been measured since 1850. Hundred-year observations of precipitation and surface runoff are available from several hydrological and climatological stations; the yields of important springs have been gauged for more than 50 years; and the national groundwater level monitoring network has been in operation for more than 35 years. Regular long-term observations enhance the accuracy of hydrological balance considerations and evaluation of both surface and groundwater resources on the national and regional levels.

Czechoslovakia's economic and social development after the Second World War and the increasing demands

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for water have led to the long-term planning, development, and management of water resources. In 1954, the Government adopted the first stage of the State Water Management Plant (SWMP) the chief focus of which was on the quantitative aspects of integrated and comprehensive use of water resources. The mounting anthropogeneous impacts on the hydrogeological system, and the subsequent deterioration of the surface and groundwater quality, led to the drafting of the second SWMP stage which was adopted by the Government in 1975. Part of the SWMP is the balance of surface and groundwater resources on the national level, including evaluation of its quality. The national territorial balance is being continuously completed with the results of hydrological and hydrogeological investigations. The second SWMP stage covers all spheres of activities in the water sector related with the country's needs and economic development. It deals with the technical, ecological, economic, forecasting, organizational, social, legislative, institutional and international aspects, and serves as the basis for the planning, development and integrated use and protection of water resources. The long-term policy and strategy of groundwater protection and quality conservation, for the benefit of the present and future generations' health, is one of the SWMP's principal objectives.

Diffuse pollution related to agricultural activities, above all the consequences of massive fertilizer application, concerns mainly deterioration in the quality of aquifers or their pollution by nitrogen compounds. Given the current fertilizer management practices, nitrogen input exceeds its uptake. This poor management, typical of many agricultural regions in the world, including Czechoslovakia, is affecting water quality and reducing the economic effectiveness of farming (*1*).

Czechoslovakia's program for groundwater protection and quality conservation with respect to the impacts of agricultural activities and the related diffuse pollution, includes the following items: identification, inventory, and risk assessment of pollution sources; groundwater quality monitoring; transport and transformation processes of nitrogen compounds in the plant-soil-groundwater system; pollutant transport modeling, particularly for the unsaturated zone; legislative aspects of groundwater protection; and health implications of nitrates in groundwater resources.

Farming as a Source of Diffuse Nitrate Pollution of Groundwater

Contemporary agriculture has changed from crop rotation to monocultures and from small-scale to mass-scale breeding of animals. The application of ever greater doses of fertilizers to farmland has resulted in conflicts between the agricultural sector and water users in many regions. In several European countries with intensive farming, a statistical relationship has been formulated as to the amount of nitrogen fertilizer applied to farmland versus nitrate contents in groundwater (*2–11*). Diffuse nitrate pollution of groundwater has been recognized to be one of the most serious impacts of farming activities on the groundwater system, in particular on shallow aquifers. However, the processes of nitrogen compounds' transport and transformation in the soil-water system are not limited only to the applied doses of fertilizers; the fertilizer nitrogen constitutes merely a small part of the total amount of nitrogen found in soil. A substantial proportion of nitrogen is bound to the soil organic mater in a state of dynamic stability. Disturbances of this stability result in a lower intensity of biochemical processes and, consequently, in higher losses of nitrogen compounds from the soil system to the hydrogeological system, thereby producing diffuse groundwater pollution.

The data available from many European regions, including Czechoslovakia, reveal that only 40 to 60% of the nitrogen fertilizer applied to arable land is removed by crops; about 25 to 30% of nitrogen is lost to the water system. Due to the great areal extent of diffuse nitrate pollution, especially in arable land having a permeable, low-thickness unsaturated zone and vulnerable aquifers, the employment of the "isolate-source-policy" and subsurface clean-up techniques approach is ineffective. The protective measures that improve groundwater quality consist of managing and controlling the nitrogen input to the plant-soil system by way of restricting or prohibiting farming activities, or by altering agricultural practices (use of suitable fertilizers, determination of the doses, times, and techniques of their application, selection of appropriate crops, and introduction of the crop-rotation system) and activities (regulation of the ratio between animal production and farmland extent and that between arable land and grassland, restriction or elimination of monocultures). The choice between the above-mentioned alternatives is largely based on economic, social, and ecological factors. In the policy- and decision-making process, the importance of groundwater resources and agricultural production for a given region should be evaluated with respect to the strategy of regional development, and the priorities and preferences concerning integrated land use planning and groundwater protection management should be established.

In regions where water supplies depend on irreplaceable groundwater resources only, less intensive agricultural production and control over all farming activities, especially in vulnerable areas of the hydrogeological system, should be strongly recommended. Restriction on agricultural activities will cause certain financial losses to farmers. The relations between the two independent systems, the physical and the economic ones, must therefore be coordinated and integrated with the objective of deriving benefits from soil and water utilization, while conserving the quality of the environment. The distribution of the benefits and costs between the water and agricultural sectors, and integrated land use planning and groundwater management are the key factors in the strategy of effective soil and water resources utilization.

In Czechoslovakia, the major sources of diffuse groundwater pollution include leakage of nitrogen compounds from the soil-plant system caused by a dramatic increase in the doses of industrial nitrogen fertilizers that are being applied to farmland. Since 1980, parallel with the hydrogeological investigation of the national territory supported by the Government and conducted for the needs of the State Water Management Plan, investigations focused on preventive protection of groundwater resources have been under way. Field trips and data collection and analysis on a regional scale are carried out for the purposes of identification, inventory, and risk assessment concerning the principal existing sources, as well as potential, site-specific and diffuse pollution sources. Investigation results are depicted in groundwater protection and aquifer vulnerability maps. Special attention is directed toward the design and operation of the soil-water quality monitoring programs, the study of nitrate occurrence, vertical and horizontal movement and distribution in the unsaturated and saturated zones, the mechanism of the transport and transformation processes in the crop-soil-water-rock system, and the modeling of changes in groundwater quality due to the effects of farming activities using mathematical simulation models. Management schemes based on sound scientific information pose a complex task of general interest and great practical importance and require a specific approach and solution in each region, comprehensive analysis of the physical and socioeconomic aspects, establishment of strategies, policies, and control measures for soil and water resources utilization, and implementation of institutional and legislative aspects and regulations.

Groundwater Quality Monitoring of Diffuse Pollution Sources

Groundwater quality monitoring, as one of the most important activities in groundwater protection and quality conservation, is a technically and financially demanding process. A groundwater quality monitoring program is governed mainly be the monitoring objectives, the extent of the territory to be monitored, and the time and spatial effects of natural processes and human impacts on the hydrogeological system. The integration and coordination of groundwater monitoring programs, in terms of both quantity and quality, with surface water, precipitation, evaporation, and soil monitoring networks is necessary because of the interrelations and the immediate and/or retarded influences existing among the water-soil components. The conjunctive design of monitoring networks and the multiple use of monitoring stations are desirable from scientific, technical, and financial points of view. Special requirements are placed on the construction of monitoring wells, as separate samples from the hydrogeological system's vertical profile are always preferred to mixed samples, which are not appropriate for the study of groundwater quality variations and contaminant hydrogeology problems. Routine monitoring of the unsaturated zone should be part of the monitoring activity too, particularly when studying the impacts of diffuse pollution.

In Czechoslovakia, national and regional groundwater quality monitoring programs are in operation. The contents of nitrogen and other types of compounds have been monitored since the early 1950s in all public water supply wells at intervals of 1 to 3 months. These wells are not included in the national groundwater quality monitoring networks, and the data obtained from them serve for decision-making and water control by regional water management authorities.

National Groundwater Quality Monitoring Network

The Czechoslovak national groundwater quality monitoring network has been in operation since 1985. It comprises three subnetworks, which include boreholes in shallow aquifers, boreholes in deeper aquifers (more than 100 m), and springs. A monitoring station for deeper aquifers operates two to three boreholes, with each one serving for the separate monitoring of the aquifers over the vertical profile of the sedimentary rock complex. For instance, in Cretaceous basins, confined aquifers in the Cenomanian are monitored separately from those situated in the overlying Middle Turonian, which are unconfined. The sampling frequency is once a year for deeper aquifers and twice a year for shallow aquifers and springs. Prior to sampling boreholes having the water level below the surface, 2 to 3 hr of pumping are obligatory. Overflowing boreholes are sampled only when double the volume of water accumulated in them flows away. When not sampled, these boreholes are closed. The analysis covers biological and chemical components included in drinking water standards, as well as selected organic compounds and heavy metals.

The national groundwater quality monitoring program is integrated with the groundwater quantity monitoring program and coordinated with the other hydrological, climatological, and pedological networks. The country's Hydrometeorological Institute is responsible for the design, operation, and maintenance of these networks. Because of the short duration of the national groundwater quality monitoring program's operation, no conclusions can be drawn as yet with respect to changes in the nitrate contents in the various aquifers on a national scale.

Regional Groundwater Quality Monitoring Program

In two regions in Czechoslovakia, marked by a high intensity of farming activities and very fertile soils that overlay productive, unconfined, and, for the greater part, vulnerable shallow aquifers located in fluvial deposits, the relations between the agro and hydro systems are observed in more detail. The areas in question are the Middle Elbe region in Bohemia and the Danube

Lowlands in Slovakia. In both of these regions, groundwater quality monitoring programs are focused on diffuse pollution due to farming activities and have been in operation for several years. The monitoring methods and system of the Bohemian regional network are presented herewith as an example.

Regional Groundwater Quality Monitoring Program in Bohemia

The regional investigation of the impact of agriculture on a shallow aquifer situated in the fluvial deposits of the Elbe River, covering an area of 3000 km^2, involves the monitoring of the areal and vertical distribution of nitrates and other compounds in groundwater and effects of natural and anthropogenic phenomena on the hydrogeological system. The area under study, with a thousand-year history of farming, is one of Bohemia's most fertile regions (Fig. 1).

Over the past 30 years, nitrate contents in groundwater under arable land have, on the average, doubled. In the same period, the amount of fertilizer applied grew almost 8-fold and cereal yields approximately doubled (Table 1). Organic fertilizers are applied once in 4 to 5 years in amounts corresponding to 200 to 250 kg N/ha, which is 40 to 50 kg N/ha annually. A total of 150 to 160 kg N/ha is used in the Middle Elbe region every year, about 30% of which is accounted for by organic fertilizers. Approximately 25 kg/year of nitrogen are contributed by precipitation and wet deposition.

FIGURE 1. Studied area: Middle Elbe region in Central Bohemia.

Table 1. Average doses of industrial fertilizers applied and average yields of winter wheat.

Year	N, kg/ha year	Wheat yields, tons/ha year
1960–1964	22.7– 34.9	3.18–2.55
1965–1969	45.3– 65.7	2.99–3.59
1970–1974	65.3– 77.6	3.48–3.97
1975–1979	88.3– 97.5	3.32–3.89
1980–1984	109.1–121.3	4.47–5.17
1985	116.9	5.42

The data available help draw a simplified nitrogen balance for part of the monitored region, which contains arable land and covers about 32,760 hectares (the District of Mělník). This balance does not include factors such as nitrogen input to the soil-plant system through sowing seed, nitrogen release from the soil reserve, and nitrogen losses due to soil erosion. For 1983, the following inputs were considered: 1876 tons of nitrogen from industrial fertilizers; 1638 tons from organic fertilizers; 327 tons through symbiotic fixation (50 kg of fixated nitrogen per hectare); and 491 tons from precipitation, totaling 5332 tons of input nitrogen. Nitrogen outputs include the following: nitrogen uptake by crops 3049 tons, denitrification 902 tons, i.e., 20% of the total nitrogen input through fertilizers. Total nitrogen outputs amounted to 3951 tons. The difference is 1381 tons, i.e., 42.2 kg N/ha year.

Under normal climatic conditions and at yields of 4.7 tons/ha year (wheat), about 25% of the nitrogen that enters the soil-plant system throughout the year remain unused in arable land. At lower yields, and thus also lower nitrogen uptake by crops, the imbalance between nitrogen inputs and outputs increases, as also the potential possibility that nitrogen will be washed out into the groundwater system.

Research has proved a low stability of shallow aquifers when faced with natural phenomena and human activities. Their response, especially to extreme climatic episodes, is quick, particulary in the aquifers' upper oxidation parts. Long-term observations have revealed that short-term, cyclic changes in the hydrogeological system are influenced by the climate. Long-term changes and the general trends of increases in nitrate content in groundwater are a response to anthropogenic influence.

Nitrate contents in the groundwater sampled from the boreholes of monitoring networks in farming areas increased from 24 mg/L (1961–1965) to 43 mg/L in 1986. In wells and well fields of water supply systems surrounded by protection zones, the nitrate increase was lower: from 21 mg/L in 1968 to 28 mg/L in 1986, with the maximum content of 43 mg/L occurring in 1981 (Fig. 2). The decline in nitrate content observed between 1981 and 1986 did not continue in 1987. According to preliminary monitoring results, nitrate contents started to increase again in 1987 due to climatic influences.

The percentage of the public water supply systems that do not meet the drinking water standards has risen from 9% in 1968 to 17% in 1986. If the current trend of nitrate content increases in shallow aquifers continues, 42% of public water supplies will not meet the drinking water standards by the year 2000 in the studied area.

Over the period from 1955–1968 to 1986, the annual increases can be estimated at 0.8 mg NO_3^- for drinking water supplies, 1.1 mg NO_3^- for boreholes of the national and regional monitoring networks, and 3.4 mg NO_3^- for shallow household wells. The lowest value of nitrate

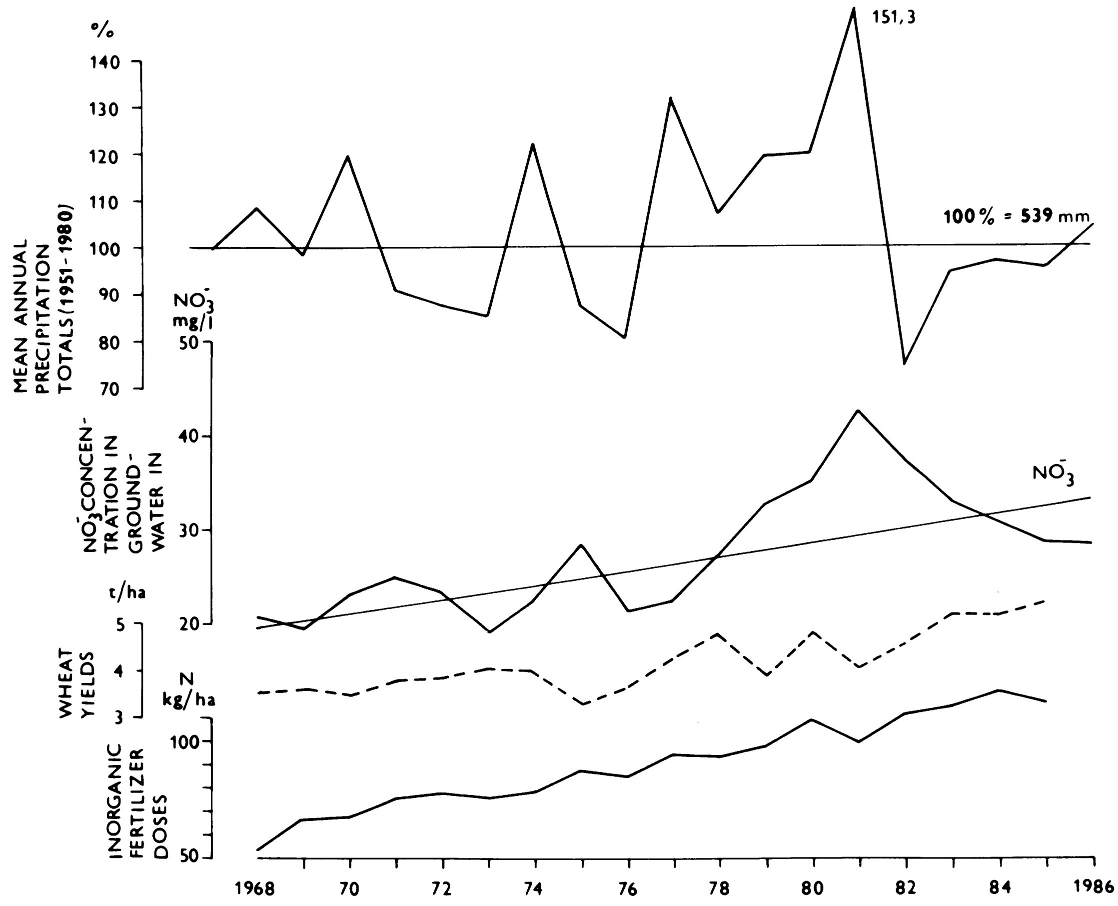

FIGURE 2. Trends of nitrate increase in shallow aquifers from 1968 to 1986.

increase in the water supply system is favorably affected by protection zones and, marginally, by water extraction from deeper aquifers. The poorer quality of groundwater in towns and villages is due to local spillages and leakages from sewage systems and septic tanks.

Over the period under review, the 1981 maximum nitrate contents in groundwater were caused by extremely high levels of precipitation (150% of the 50-year mean) in 1981 and during the preceding years. When merely 1 year rich in precipitation (for instance 1970, 1974, 1977), with extreme precipitation toward the end of the year, followed years with poor precipitation, the latter's effect on nitrate contents in the shallow aquifer was retarded and became manifest only during the year that followed the wet one.

The 1982 climatic situation and the 1983 to 1985 below-average precipitations had both significantly affected the groundwater system and the nitrate values in the shallow aquifer in 1983 to 1985 (Fig. 3). The low precipitation in 1982 (70% of the normal long-term mean) and weather conditions favorable for cereal growth in that and the following years resulted in a marked decline of nitrate content in groundwater. The nitrogen was taken up by high yields, the intensity of nitrification processes dropped due to a low soil water content, and the medium was lacking for nitrogen to be transported to the saturated zone. Analogous responses by the hydrogeological system to precipitation deficits were also observed in the 1971–1973 and the 1975–1976 periods. The aquifer's quick response to natural and anthropogenic impacts is positive in the sense that if agricultural activities and groundwater protection are mutually optimized and under control, realistic possibilities will exist for a rapid restoration of the hydrogeological system's quality. On the other hand, the system's fast response has also some negative consequences because it signals the groundwater's easy vulnerability and the possibility of a rapid deterioration in its quality.

The dominant role played by agricultural activities with respect to nitrate contents in groundwater can well be observed from comparison with forested areas. In the 1968 to 1985 period, the nitrate content in groundwater under forested land was of the order of units of milligrams per liter only.

Distinct differences have been registered between the groundwater quality in areas with overlaying clayous soils (30 mg/L NO_3^-) and in those covered by sandy soils (64 mg/L NO_3^-). Investigations have also confirmed

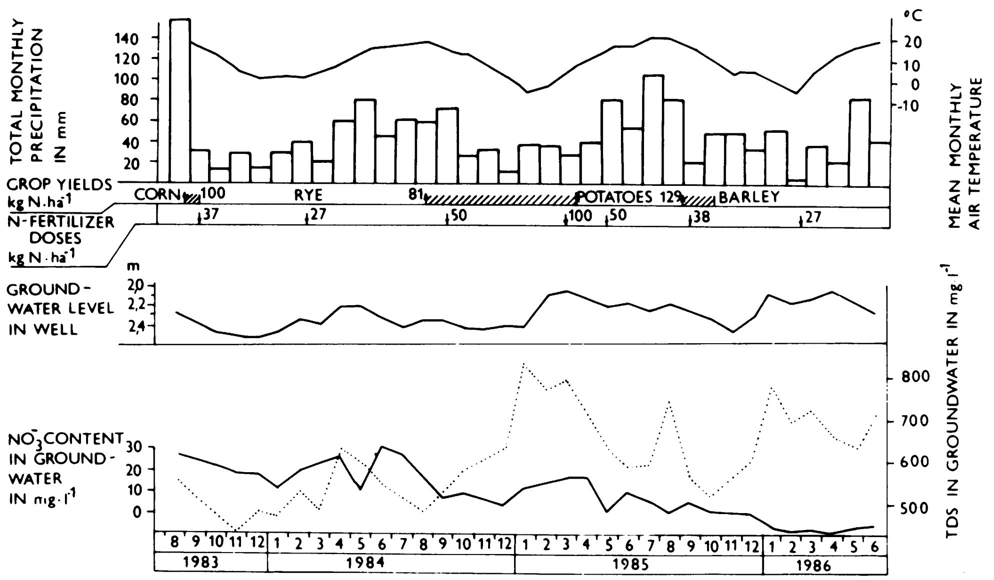

FIGURE 3. Seasonal fluctuations of nitrate content in shallow aquifer.

the vertical hydrochemical zonality and heterogeneity of shallow aquifers. A decline in nitrate content is apparent toward the base of the aquifer. The slow, vertical downward flow was evidenced by tritium analyses. In the lower parts of the aquifer, reduction conditions prevail which, combined with microbial processes, cause reduction of nitrate to ammonium ions and increases in the content of bivalent iron. Nitrate, sodium, and potassium contents also decline in the aquifer's vertical profile. In the saturated zone, nitrates move vertically at a rate of 0.1 to 0.4 m/year.

With the increase in the aquifer's nitrate content, that of chlorides, sulfates, calcium and, frequently, iron and ammonium ions increases too. This rise is produced by the gradual acidification of the environment (sulfur and calcium), reduction conditions in the aquifer (iron, ammonium ions), and the growing intensity of anthropogenic influences (chlorides). In shallow aquifers, increased nitrate contents mostly occur in their upper, oxidation parts, which is a favorable factor for their utilization as water supply sources, this assumes water extraction from the aquifers lower part only and that the groundwater flow in the anisotropic aquifer is horizontal. This requires that the quantities of pumped water be adequate to the aquifers' hydrogeological and hydraulic properties. Thus, monitoring the vertical hydrochemical profile of aquifers is of practical importance for groundwater exploitation and protection in farmland areas.

Transport and Transformation Processes of Nitrogen Compounds in the Soil Groundwater System

The transport and transformation processes of nitrogen compounds in the soil-groundwater system are the subject of a study conducted at the 30-ha Samšín experimental station (Fig. 1). Its land is divided into several plots, each under different conditions of fertilization. This experimental station is situated in the Czech-Moravian Highlands, on a gentle slope (2–5°), at an altitude of 490 to 520 m. In this region, paragneiss is the most prevalent bedrock. On the experimental site, it is weathered to a depth of 2 to 6 m, forming partially redeposited sands. On this rock substrate, dystric combisols have developed, having characteristics as listed in Table 2.

The groundwater level conforms to the inclination of the terrain, and its depth ranges from 2 m (at the bottom part of the plot) to 6 m under the surface (in the upper part of the plot). The long-term average annual precipitation amounts to 717 mm (63% of which occurs in the vegetational season) and average total runoff is 306 mm (20% of which is subsurface runoff). The long-term average annual temperature is 6.8°C, and 13.1°C in the vegetational season.

A modified sowing procedure had been adopted for the experiments, with 67% cereals, 11% root crops, and 22% fodder between 1976 and 1985. For the cereals, doses of 70 or 140 kg N/ha year were applied to the individual experimental plots through different types of

Table 2. Soil characteristics at the Samšín experimental station.

Characteristic	Value
Proportion of soil particles smaller than 0.001 mm, %	4.1
Soil particle density, kg/m^3	2650
Bulk density of soil, kg/m^3	1400
Bulk density fraction grain less than 1 mm, kg/m^3	1000
Full soil water capacity, %	45.8
Water retention capacity, %	22.5
Wilting point, %	12.0
Usable water capacity, %	9.7

fertilizer (ammonium nitrate with limestone, ammonium sulfate, and ammonium nitrate with urea). Root crops were fertilized by the same type of inorganic fertilizers as well as with farm manure. On the contrary, the doses of nitrate fertilizers were reduced for the fodder to 40 kg N/ha in 1984 and to 0 kg N/ha in 1985. A new experimental cycle was started in the autumn of 1985 and is still under way.

Apart from the effects of the different regimes of inorganic fertilizer application, the research was also focused on the study of those produced by disturbed dynamic stability of the soil organic matter on the increases in nitrate content in groundwater. This phenomenon is frequently observed in areas with intensive farming activities.

A significant indicator of the soil organic matter's state is the carbon/nitrogen ratio. For the soil with stabilized organic matter this ratio is 25 to 30:1, which approximately corresponds to a C_{ox}:N_{tot} ratio in soil of 10:1 (*12*). When C:N is greater than 10, the free nitrate ions are immobilized by the microbial biomass; when C:N is less than 10, the ammonia NH_4^+ released during mineralization processes is utilized by heterotrophic microflora for protein synthesis, and its surplus is oxidized to NO_3^- by nitrification bacteria. The intensity of these processes depends mainly on: *a*) the soil hydrothermal conditions (temperature, initial and incubation moisture); *b*) the composition of organic and inorganic soil components; *c*) the CO_2 content in the soil atmosphere; *d*) the amount of remineralized NH_4^+ needed in nitrification processes; and *e*) the sowing procedure, the types and doses of organic and inorganic nitrogen fertilizers, the technique of soil cultivation.

The content of mobile nitrogen in the soil layer of the experimental plots A and B was monitored. It has been found that the part of nitrogen that is washed out from the unsaturated zone into groundwater in early spring was mobilized in the preceding autumn. This process is controlled by the dynamics of the microbially accessible carbon and nitrogen, which affects the intensity of nitrogen mobilization and immobilization processes (Fig. 4).

Under the conditions prevailing in Central Europe, the microbial activity in soil usually increases two times in a year: in spring when the soil temperature rises as the soil moisture gradually declines close to the optimum value (60% of the full water capacity); and in autumn when the soil still retains sufficient temperature and, due to lower evaporation, adequate moisture (*13*). In these periods, intensive microbial activity is manifest by increased respiration, which leads to a decline in the content of microbially accessible carbon substrates in soil. Their deficit in relation to the content of the microbially accessible NH_4^+ ions determines the potential intensity of nitrification processes.

The NO_3^- released by these processes is used by plants in the spring. The degree of its utilization depends strongly on climatic factors. In autumn, when no intermediate plants are sown, nitrogen uptake from the soil or its microbial immobilization in soil by plants do not occur. If no organic fertilizers are applied after crop harvesting, the deficit of organic substances in soil increases. Thus, theoretically, conditions are created for the leaching of nitrates into the deeper parts of the unsaturated zone. On the other hand, in virgin land, the substantial part of the vegetational cover remains

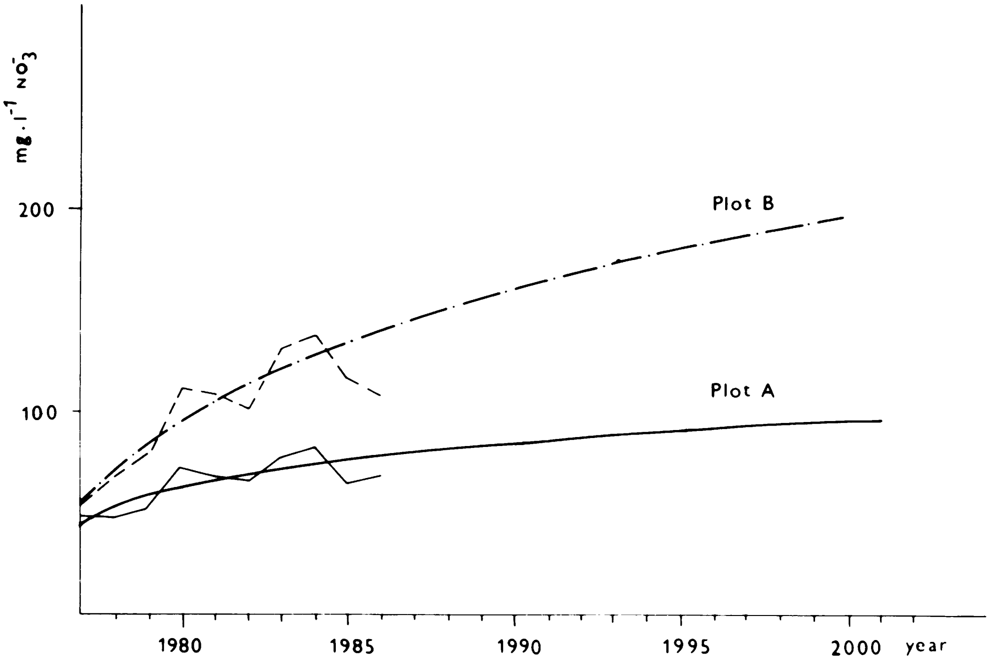

FIGURE 4. Nitrate content increases in groundwater of experimental plots A and B.

in place, and conditions for microbial immobilization of nitrogen are satisfied. Nitrogen leaching from soil to the underground is reduced.

The long-term research into nitrogen circulation on the experimental plots and its approximative balance have shown that the long-term stabilization of nitrate content in groundwater does not merely depend on the amount of nitrogen fertilizer applied. Even when only 70 kg N/ha year was used, which is a low dose for intensive farming, the nitrogen content in groundwater did not stabilize (Fig. 4).

The apparent inconsistency between the high variability of the nitrate nitrogen content in the soil of plot A (Fig. 5) and the long-lasting lower average increase in groundwater under the same plot (Fig. 4), is caused by the different dynamics of the nitrogen cycle that is controlled, particularly, by the content of microbially accessible nitrogen and carbon.

The concentrations of these elements can be expressed indirectly by the value of the NG:B test, i.e., the ratio between soil microorganism respiration (after the addition of ammonium nitrogen and glucose) and basal respiration. High values of this test (>20) signal a deficit of microbially easily accessible nitrogen/carbon substances in the soil; low values (<15) indicate either a sufficient amount of these substances (at a high intensity of basal respiration) or a low amount of microflora in the tested soil.

The difference in the dynamics of the nitrogen cycle in the two plots A and B is expressed in Fig. 6. In the soil of plot A, under long-term fertilization by lower doses of inorganic nitrogen fertilizer, the dependence

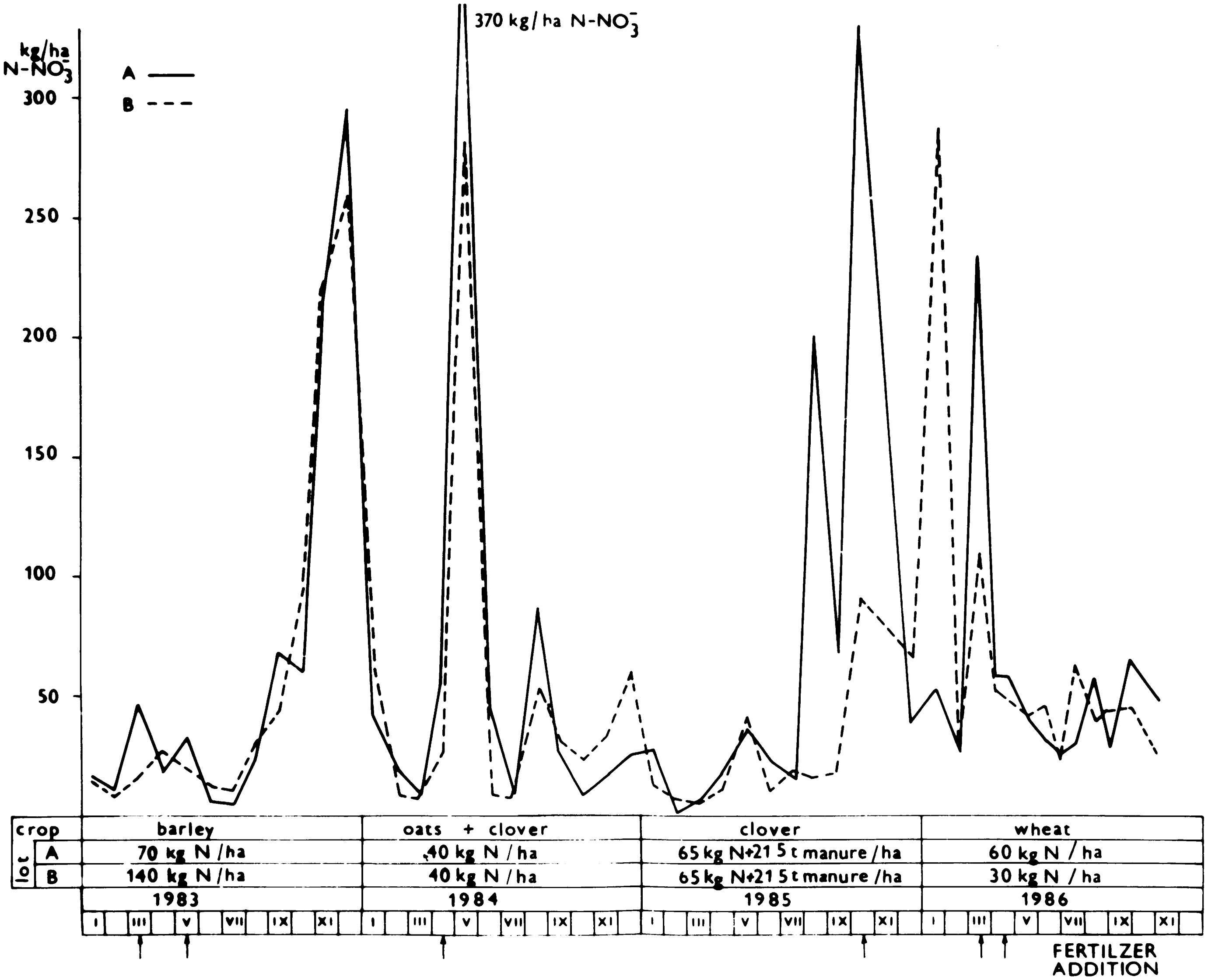

FIGURE 5. Nitrate nitrogen contents (N–NO_3^-) in soil on experimental plots A and B.

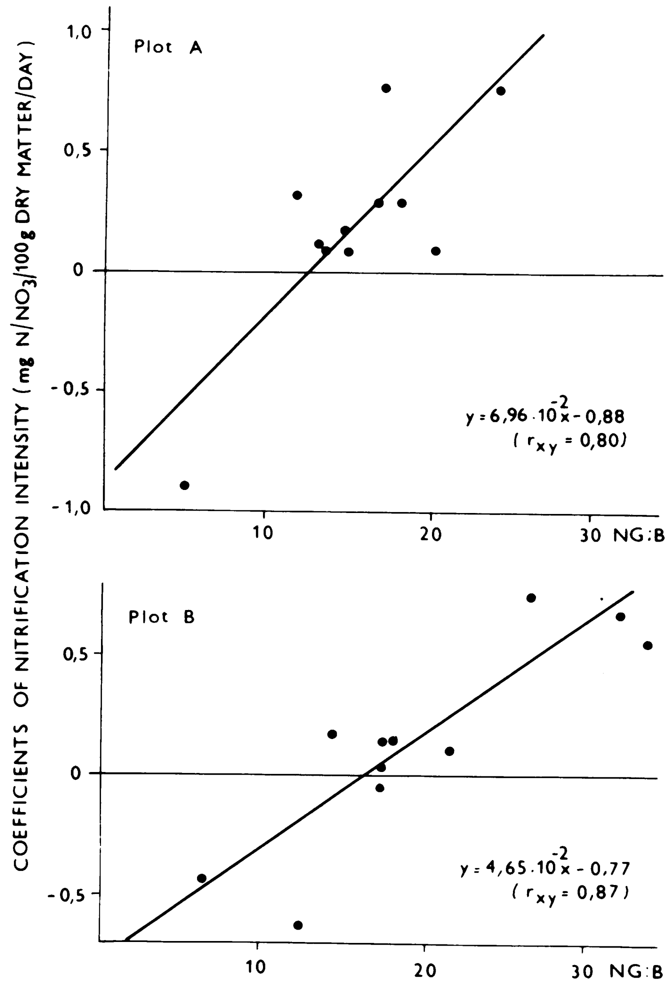

FIGURE 6. Relation between nitrification intensity and NG:B parameter-moisture interval 50 to 80% of the full water capacity.

of the intensity of the mobilization and immobilization processes on changes in the NG:B parameter is sharper than in plot B. This means that in the soil of plot A, changes in the organic matter composition and soil biomass mortality reflect in the nitrogen mobilization and immobilization cycle much more distinctly. This difference between the compositions of the soil organic matter in the studied plots mirrors the difference between the doses and kinds of fertilizers. In plot A, the composition of the soil organic matter is more favorable in terms of its effects on the groundwater quality, since the possibilities for nitrogen leaching from soil are reduced.

The approximative balance equation for nitrogen in plot A shows that on the long-term scale, the nitrogen needed for biomass production is supplied not only by fertilizers but also by the nitrogen released during the soil organic matter mineralization 1983 to 1986 period, values in kilograms nitrogen per hectare year:

$$\begin{array}{ccccccccccccccc} N_v & + & N_o & + & N_d & = & N_d & + & N_f & + & N_m & + & N_s & + & N_{nz} \\ 150 & + & 45 & + & 25 & = & 84 & + & 35 & + & 90 & + & 11 & \pm & 0 \end{array} \qquad (1)$$

where N_v is the nitrogen uptake by the upper part of vegetation, determined by analysis (*14*); N_o is the nitrogen runoff in ground and surface water, determined by measurements and analysis; N_d is the nitrate nitrogen ($N-NO_3^-$) losses through denitrification in the unsaturated zone, determined by analysis and measurements; N_h is the amount of nitrogen applied in inorganic and farm fertilizers, determined by weighing and analysis; N_f is the amount of nitrogen bound by symbiotic bacteria, estimate based on plant (clover) and soil analysis; N_m is the amount of nitrogen mobilized during soil organic matter mineralization: nitrified N − immobilized N + denitrified N; determined on the basis of microbial tests (*15*); average intensity of mobilization/immobilization processes: + 8.2 × 10^{-3}g $N-NO_3^-$/day 100 g dry matter; N_s is the amount of nitrogen from precipitation, determined by measurements and analysis; and N_{nz} is the changes in nitrogen stores (reserves) in the unsaturated zone.

The intensity of the processes that take place in the nitrogen mobilization/immobilization cycle has been determined using the nitrification constants of soil samples. The analysis has proved the considerable importance of these processes for the total balance of nitrate nitrogen, especially in spring and autumn. The methods employed and the sampling frequency (once a month) did not allow a sufficiently accurate separation of immobilized and denitrified nitrogen.

The intensity of denitrification over the unsaturated zone's profile was determined on the basis of the $NO_3^- - N$ and Cl^- ion content and their ratio in samples taken from deposits of the unsaturated zone and in groundwater samples taken from plot A. In the nonvegetational season in the recharge period, the $NO_3^- - N/Cl^-$ ratio was 1.5 to 3.5 over the 0.0 to 0.3 m soil profile. Higher nitrate contents were usually indicated in the upper, more aerated layers. The $NO_3^- - N/Cl^-$ ratio in groundwater ranged from 0.5 to 0.6.

Over the unsaturated zone's profile, due to the decreasing permeability and porosity, the concentration of chlorine and nitrate nitrogen decline with increasing depth (Fig. 7). At the groundwater table level, 2.5 m under the surface, their concentration ($NO_3^- - N/Cl^-$ = 0.58) was about 60% lower than their relative average content in the soil layer ($NO_3^- - N/Cl^-$ = 1.46).

The vertical stratification of both components was extrapolated using the relation

$$y = ax \exp [b] \qquad (2)$$

Where y is the concentration of element (in mg/100 g dry matter) at depth x (m), and a,b are experimentally determined constants. The values for plot A were found to be

	a	b	r^2_{xy} (coefficent of determination)
$N-NO_3^-$	0.81	-0.45	0.72
Cl^-	1.02	-0.10	0.31

(2a)

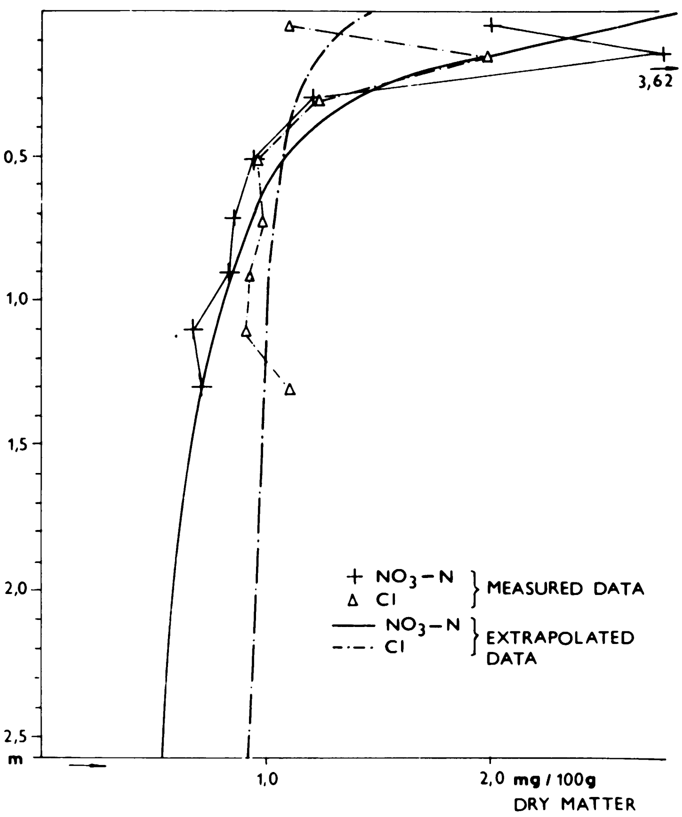

FIGURE 7. N-NO_3^- distribution in the vertical profile of the unsaturated zone—experimental field, plot A (average values).

Except for the denitrification processes, the mechanisms of Cl^- and NO_3^- ions' transport in the unsaturated zone are identical. Assuming that the 60% losses of nitrogen based on the $NO_3^- - N/Cl^-$ ratio in the unsaturated zone are largely accounted for by denitrification processes, the nitrogen losses due to denitrification can be estimated at about 25 kg N/ha year. The remaining 40% of nitrogen (about 17 kg N/ha) flow away with the ground water.

Integrating Eq. (2) over the 0.0- to 2.5-m interval, the nitrate nitrogen reserve in the unsaturated zone was determined to be approximately 250 kg/ha.

For the same period (1983–1986) and the same plot A, an approximate balance of organic carbon was estimated. Average annual carbon losses due to soil organic matter mineralization, based on respiration tests, were estimated at 800 kg/ha. Some 550 kg/ha of post harvest cereal residuals transform into humus on the experimental plot. The carbon balance was improved by sowing intermediate plants leaving more post-harvest remains and by organic fertilizing in 1985. Average values of carbon in kg/ha for the 1983 to 1986 period are expressed in Eq. (3):

$$\begin{array}{ccccccc} C_r & \pm & C_z & = & C_{pz} & + & C_{oh} \\ 800 & \pm & 225 & = & 600 & + & 425 \end{array} \tag{3}$$

where C_r is the amount of soil organic carbon consumed for soil microorganism respiration, estimated by microbiological analysis; C_{pz} is the organic carbon from post-harvest remains, estimated by soil analysis; C_{oh} is the organic carbon from farm manure, estimated from the dose applied: and C_z is the changes in organic carbon content in arable soil during the period under consideration.

In the period under review, the nitrate content in the groundwater of the experimental plots was primarily affected by changes in the carbon balance (rise in carbon content due to organic fertilizing and clover cultivation). The nitrogen content in groundwater grew also in 1984 when the dose of inorganic nitrogen fertilizer was only 40 kg N/ha year. The increase in nitrate content was caused by the high intensity of nitrification processes in the spring of 1984 and, partially, also by the retardation effect of the unsaturated zone. A decline in nitrate concentration in groundwater was observed as late as 1985.

This favorable declining trend of the nitrate content in groundwater continued also in 1986 thanks to a change in the management of inorganic fertilizer application and an adequate increase in the content and quality of carbon substrates in the soil (1984: 1.29% C_{ox}, leave in humic/fulvic acids 0.84; 1986: 2.67% C_{ox}, r humic/fulvic acids 0.62). However, the optimum dynamic stability of the soil system has not yet been attained on the experimental plots. Research results show that the restoration of the soil-groundwater system is a complicated process that usually requires changes in the extent and intensity of agricultural activity, as well as consistent attention to natural conditions.

It has been pointed out that the nitrogen and carbon balance is essential for gaining insight into the physical, chemical, and biological processes that take place in the unsaturated zone. These processes strongly control the amount of nitrogen leached into the saturated zone. Perturbation of the organic carbon and nitrogen balance in soil, with consequences for the groundwater quality, occurs especially when the traditional crop rotation is replaced by monocultures. Over a period of 4 years, at the same intensity of fertilization, the nitrate content increase in the experimental plots' groundwater under monoculture (barley) was nearly twice as high as in plots with traditional crop rotation (potatoes, wheat, barley, oats, and clover).

The nitrogen balance equation indicates that for a long period of time, excessive amounts of nitrogen have been supplied to the soil through fertilization; this is reflected in the instability of the soil organic matter and in considerable losses of nitrogen into the groundwater system. However, research has also revealed the significance of short-term changes for the total nitrogen balance due to the immobilization and denitrification processes within a 1-year cycle. Monitoring of soil-groundwater quality, with a high frequency of sampling in the early spring period, is therefore especially emphasized for European climatic conditions.

Pollutant Transport in the Unsaturated Zone—Model Verification and Input Data

Deterministic Model

The deterministic transport models that describe pollutant behavior in the unsaturated zone are based on the classical convection-dispersion equation. The latter usually assumes solute transport by convection and hydrodynamic dispersion, sorption/desorption of solute to solid particles of the porus medium, and changes in concentrations due to chemical, microbial and other types of reactions.

For prognostic calculations of nitrate transport the WASTEN mathematical model (*18*) was used. This model can be considered to be representative of deterministic hydrodynamic models. The various models differ from each other in some not too essential details: mathematical form of the description of retention curves, unsaturated hydraulic conductivity and coefficients of hydrodynamic dispersion, description of the kinetics of individual reactions, and the numerical techniques for calculating the basic equations.

Water Flow Submodel

The WASTEN model permits the computation of the vertical transient isothermal regime of water flow in an unsaturated stratified medium. The one-dimensional regime of flow is described by equation

$$c(\theta)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z}\right] - \frac{\partial(K(h))}{\partial z} - A(z,t) \qquad (4)$$

where $c(\theta) = \partial\theta/\partial h$ is the differential water capacity (m^{-1}); θ = volumetric soil moisture (m^3/m^3); h = soil water potential (m); K(h) = unsaturated hydraulic conductivity (m/sec); z = vertical coordinate (m); and A(z,t) = water uptake by plants ($m^3/sec\ m^2$).

Soil Water Potential

The relation between the soil water potential and the soil water content is described by equation:

$$\theta(h) = \frac{\theta_s}{\left[1 - \left(-\frac{h}{a}\right)^b\right]} \qquad (5)$$

where θ_s is saturated soil moisture (m^3/m^3); and a,b are parameters which specify the soil.

Unsaturated Hydraulic Conductivity

The value of the coefficient of the unsaturated hydraulic conductivity with respect to the soil moisture is taken in the exponential form

$$K(\theta) = \eta \exp(\alpha\theta) \qquad (6)$$

where α, η are parameters that specify the soil.

Water Uptake by Plant Roots

The vertical distribution of water uptake by plant roots can be expressed as

$$A(z,t) = \frac{T\,R(z)\,K(h)}{\int_0^z R(z)K(z)dz} \qquad (7)$$

where z = depth of the root system (m); T = evapotranspiration rate (m/sec); and R(z) = distribution function of the root system.

The distribution function of the root system can be described by the exponential equation

$$R(z) = a\exp(-bz) \qquad (8)$$

where a,b are parameters that depend on the type of plants, vegetational season and soil.

Submodel of Transport and Transformation Processes

The transport of ammonium nitrogen is taken as

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - \frac{v}{\theta}\frac{\partial c}{\partial z} - k_1 c - q_{N\text{-}NH_4^+} \qquad (9)$$

and that of nitrate nitrogen as

$$\frac{\partial y}{\partial t} = D\frac{\partial^2 y}{\partial z^2} - \frac{v}{\theta}\frac{\partial y}{\partial z} - k_1 c - k_2 y - q_{N\text{-}NO_3^-} \qquad (10)$$

where c = concentration of ammonium nitrogen (mg/L); y = concentration of nitrate nitrogen (mg/L); D = coefficient of hydrodynamic dispersion (m^2/sec); R = $(1 + \frac{\rho}{\theta}K_d)$ = retardation factor; v = water flow velocity (m/sec); k_1 = velocity constant for nitrification (sec^{-1}); and k_2 = velocity constant for denitrification (sec^{-1}).

Hydrodynamic Dispersion

The WASTEN model assumes the coefficient of hydrodynamic dispersion in the simplest form—a constant value independent of water flow velocity or soil water content.

Nitrification and Denitrification

The processes of nitrification and denitrification are described in the model by a first-order kinetic equation:

NITRIFICATION

$$\frac{\partial c}{\partial t} = k_1 c \qquad (11)$$

DENITRIFICATION

$$\frac{\partial y}{\partial t} = k_2 y \qquad (12)$$

The velocity constants k_1 and k_2 depend on the soil water potential and the soil water content, respectively.

Nitrogen Uptake by Plants

Nitrogen uptake by plants is expressed by means of the Michealis-Menten kinetic equation:

$$q_{N\text{-}NH_4^+} = \frac{I_{max}c}{K_m+c+y} \; ; \; q_{N\text{-}NO_3^-} = \frac{I_{max}y}{K_m+c+y} \qquad (13)$$

The flow Eq. (4) and the transport Eqs. (9) and (10) are solved using the method of finite differences.

Model Verification

The simulation model calculations have been verified for input data obtained by means of laboratory and field measurements at the Nová Ves experimental station (Fig. 1). This station is situated at the fringe of the Czech Cretaceous Basin. Here, Upper Chalk comprises fine clayey sandstones and Cenomanian siltstones, while quarternary deposits are formed by a layer of loess loam. On this rock base, brown, illimerate, locally plano soils have developed.

Under the pedological conditions prevailing at the experimental station, in the natural regime of precipitation and with industrial fertilizers applied in an extent that is normal for this region, the transport of agrochemicals is slow. The verification of the model calculations involved an infiltration/tracer test at the station. A large-area infiltrometer having an active surface of 6.5 m^2 and an outer ring 50 cm wide was used for the test. The infiltrometer was void of vegetation.

A concentrated solution of the NPK complex fertilizer was used for the infiltration test. The ammonium and nitrate nitrogen were concentrated at 2750 mg/L. The solution was dosed into the infiltrometer lines with PVC foil. At the moment of starting the infiltration, the foil was removed from the infiltrometer. A total of 100 mm of the solution was infiltrated.

Prior to the test, the soil profile was sampled to find the initial vertical distribution of soil water content and the concentration of $N - NO_3^- = N - NH_4^+$; a reference sample was taken from the infiltrometer as well. The soil was further sampled for chemical analysis during the infiltration test.

Input Data

In the first run of the simulation calculations, the data obtained largely by means of laboratory measurements on samples of soil taken at the station were used.

Soil Water Head

The required parameters of the retention curves were determined through measurements on intact soil sam-

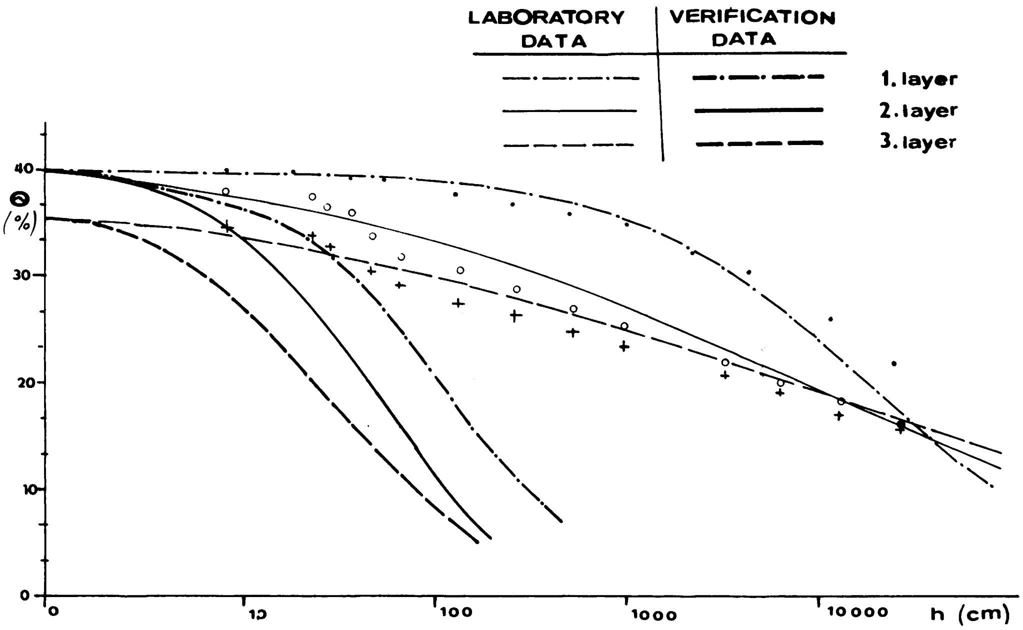

FIGURE 8. Retention curves, measured in laboratory and following model verification.

ples on Temps cells in the dewatering regime. Hysteresis of the retention curves was neglected. Results of these measurements and their evaluation are shown in Figure 8.

Unsaturated Hydraulic Conductivity

Laboratory measurements helped determine the values of the unsaturated hydraulic conductivity. Using Marshall's relations (*17*), the relations between hydraulic conductivity and the soil water content were computed from the parameters of retention curves (Fig. 9).

Coefficient of Hydrodynamic Dispersion and Sorption

These parameters were measured on a column in both stationary and nonstationary regimes of flow. A solution of 0.1 N $MgCl_2$ was used as tracer. The results were evaluated according the van Genuchten (*16*). The dispersion curves measured were practically identical for both Mg^{2+} cations and Cl^- anions. The effect of sorption did not show here, due to the soil's acid reaction with pH around 5.

Nitrification

The velocity constant of the nitrification process that is described in the model by a first-order kinetic expression was determined by means of nitrification tests. The duration incubation time of these tests was 8 days, and their results were evaluated with the help of expression

$$k_1 = -1.446 \times 10^{-6} \ln \frac{c_8}{c_0} \tag{14}$$

where c_0 is the initial concentration $N-NO_3^-$ (mg/L); c_8 is concentration of $N-NO_3^-$ in 8 days (mg/L); and k_1 is the velocity constant (per sec).

Denitrification

Our study did not include the denitrification process. For model computations, the value of coefficient k_2 was adopted from the work of Selim and Iskandar (*18*). This process, too, was described by a first-order kinetic expression.

Nitrogen Uptake by Vegetation

Since the infiltrometer had been void of vegetation, nitrogen uptake was not considered in model verification using the infiltration test.

Initial Vertical Distribution of the Soil Water Content and Nitrogen Concentration

The initial vertical distribution of the soil water content was found through laboratory measurements

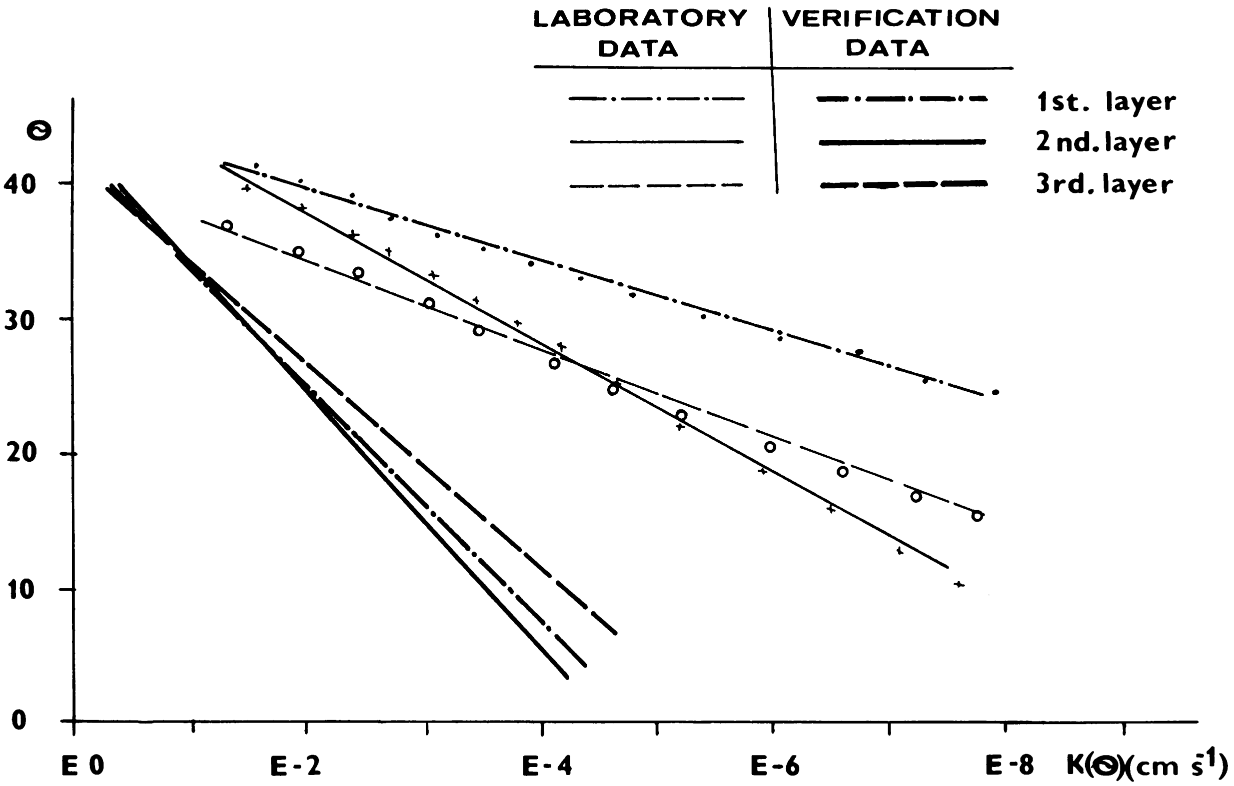

FIGURE 9. Unsaturated hydraulic conductivity, determined in laboratory and following model verification.

(gravimetrically) on soil samples taken with the help of a hand-operated auger. Subsequent measurements of the soil content were carried out directly in the borehole using a capacity sounding device.

The initial vertical distribution of the concentration of ammonium and nitrate nitrogen was determined by chemical analysis of soil samples. The vertical distribution of $N - NO_3^-$ concentration prior to the infiltration test is shown in Figure 10.

Model Verification

In the first version of model calculations, input data obtained by laboratory measurements were used. The values of individual parameters are summarized in Table 3.

The computed vertical distribution of NO_3^- concentration is depicted in Figure 10. It is obvious from this figure that there is a great disproportion between the values computed by the model and those measured *in situ* during the infiltration test, which are also plotted in the figure.

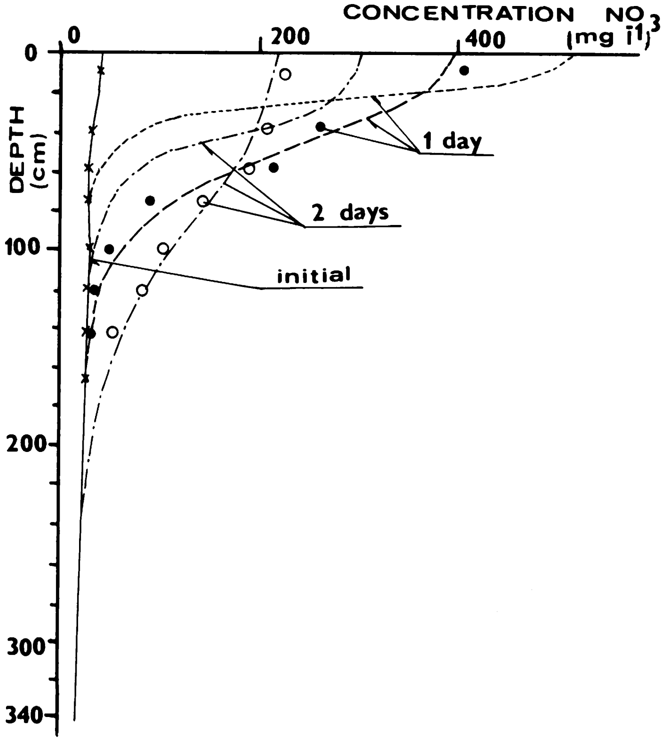

FIGURE 10. Vertical distribution of $N - NO_3^-$ concentrations as measured during the infiltration test and calculated from laboratory data and those for the verified model.

Table 3. Input data for model calculations as determined in the laboratory.

Layers	η	α	a	b	θ_s	k_1	k_2
1	0.59×10^{-17}	89.0	0.2×10^5	0.70	0.40	0.1	0.01
2	0.11×10^{-9}	49.0	0.15×10^5	0.35	0.40	0.0	0.0
3	0.24×10^{-12}	71.0	0.20×10^5	0.30	0.36	0.0	0.0

By way of gradually modifying input data values (parameters of retention curves and unsaturated hydraulic conductivity), the vertical profiles of NO_3^- concentration distribution were computed, which approximate the measured values. The input data corresponding to this resulting version of computations are listed in Table 4. Retention curves and the unsaturated hydraulic conductivity for the verified model solution are shown in Figures 8 and 9.

Comparing the values of the parameters of the transport processes and those used in the verified version of the model, it is evident that for a routine usage of the model the results yielded by laboratory measurements of the retention curves and the unsaturated hydraulic conductivities cannot be interpreted.

Model Application

Practical application of the model is demonstrated on nitrogen behavior in soil using industrial fertilizers: ammonium sulfate and potassium nitrate with limestone.

The use of fertilizers was considered in the nonvegetational season, as well as in the season of the vegetation's optimum growth. In these computations, the data obtained from the infiltration test along with other laboratory and field data were used.

Input Data

The physical characteristics of soil are summarized in Table 4.

Infiltration of Precipitation Water and Dissolved Fertilizers

Inorganic fertilizers were applied to the soil's surface in the powder form and dissolved in precipitation or irrigation water. A part of the fertilizers contained in the solute was transported into soil, another part was washed away in surface runoff to surface streams, and the last part, undissolved, remained on the soil's surface.

It is difficult and time-consuming to study the precipitation-runoff relations and the transport process under natural conditions. There is only a low probability that the moment of fertilizer application would coincide with precipitation having sufficient intensity to cause surface runoff. Therefore a laboratory test was carried out for the purposes of this study.

A sample of soil was placed in a 50 × 50-cm^2 sampler, with surface inclined at 3%. Rainfall of the required intensity and duration was produced by a laboratory precipitation simulator. This device made it possible to

Table 4. Input data for verified model calculations.

Layers	η	α	a	b	θ_s	k_1	k_2
1	1.12×10^{-5}	26.0	0.12×10^3	1.0	0.40	0.12	0.01
2	0.20×10^{-5}	24.0	0.37×10^2	1.0	0.40	0.0	0.0
3	0.22×10^{-5}	34.0	0.26×10^3	1.0	0.36	0.0	0.0

generate arbitrary model precipitations, including the required flow of kinetic energy. Two precipitation intensities, 1.0 and 1.5 mm/min, were selected for the experiment. Powder fertilizers, ammonium sulfate, and potassium nitrate with limestone were used for testing, in equal doses of 70 kg N/ha. The distribution of fertilizers in the infiltrated water, the surface runoff and the undissolved form on the soil's surface were determined by on-line sampling and analysis of water in the surface runoff, the infiltrated water and the soil sample during the experiment. The results of these measurements are listed in Table 5.

Evapotranspiration

The rate of evapotranspiration was calculated on the basis of climatic and meteorological data collected by the station's met service. The value of evapotranspiration was found with the help of Penman's equation. For the period under review, the value 2.5×10^{-6} m/day was registered.

Nitrogen Uptake by Vegetation

By way of sampling and analyzing the vegetation, the dynamics of nitrogen uptake by vegetation was systematically being determined during the vegetational season and then described by the empirical expression

$$Q = \frac{A \exp(ct + b)}{1 + \exp\left[(ct + b)^2\right]} \tag{15}$$

where t denotes the time elapsed from the beginning of the vegetational season (days); and A,c,b, are coefficients depending on the soil, temperature, nutrient content, etc.

This relation is plotted for barley and wheat in Figure 11. For the simulation period, the maximum nitrogen uptake was determined at $I_{max} = 2.1 \times 10^{-8}$ mg/cm day. The Michaelis constant was taken as $K_m = 1$.

The distribution function of the root system density was assumed in the form

$$R(z) = 227 \exp(-0.1z) \tag{16}$$

where z denotes the depth under the soil's surface (m).

Nitrification and Denitrification

The values of the nitrification velocity constant were found by means of the nitrification test and evaluated with the help of Eq. (4). In the simulation computation, the value $k_1 = 4.6 \times 10^{-4}$ day^{-1} was used. The value of the denitrification velocity constant was adopted from the work of Selim and Iskandar (*18*), i.e., $k_2 = 2.1 \times 10^{-4}$ day^{-1}.

Table 5. Distribution of inorganic fertilizers, ammonium sulfate (AS) and potassium nitrate with limestone in the surface runoff, infiltrated water, and undissolved phase on the soil's surface.

	N in surface runoff		N in infiltrated water		N in undissolved phase on surface	
	mgN	%	mgN	%	mgN	%
Rain intensity, 1.50 mm/min						
Ammonium sulfate	24.08	13.37	1311.50	75.01	204.42	11.62
Potassium nitrate limestone	112.25	6.40	1504.92	86.01	132.83	7.59
Rain intensity, 1.00 mm/min						
Ammonium sulfate	170.63	9.72	1490.51	79.51	188.55	10.77
Potassium nitrate limestone	109.06	6.24	1504.37	85.96	136.57	7.80

Initial and Boundary Conditions

The soil profile under study was divided into three layers: $L_1 = 32$ cm; $L_2 = 34$ cm; and $L_3 = 272$ cm. The initial vertical distribution of the soil water content and the $N-NO_3^-$ and $N-NH_4^+$ concentrations was assumed the same as for the model verification.

Simulation Outputs

An example of the simulation results can be seen in Figures 12 and 13. These figures indicate the time/space development of $N-NO_3^-$ concentration in the soil profile, with potassium nitrate and limestone applied to the soil's surface void of vegetation as well as at the time of the optimum growth of vegetation. Both figures suggest that fertilizer application in the nonvegetational season is not suitable. During this period nitrates penetrate the soil profile to greater depths, thereby suggesting that the risk of groundwater contamination is greater than if vegetation was present.

Validity of Model Calculations

The practical applicability of deterministic transport models for the description of pollutant behavior in the unsaturated zone depends on the validity of the results

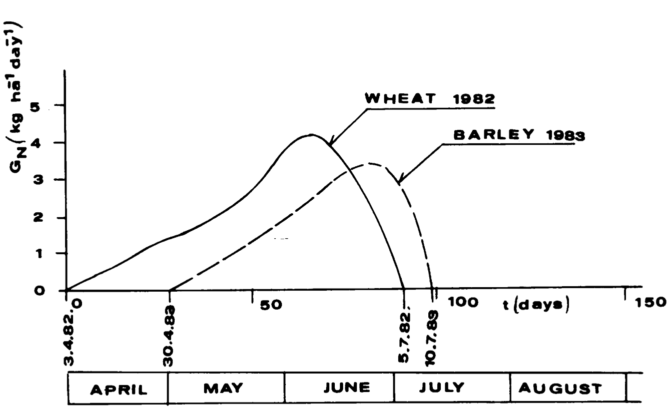

FIGURE 11. Nitrogen uptake by vegetation in time.

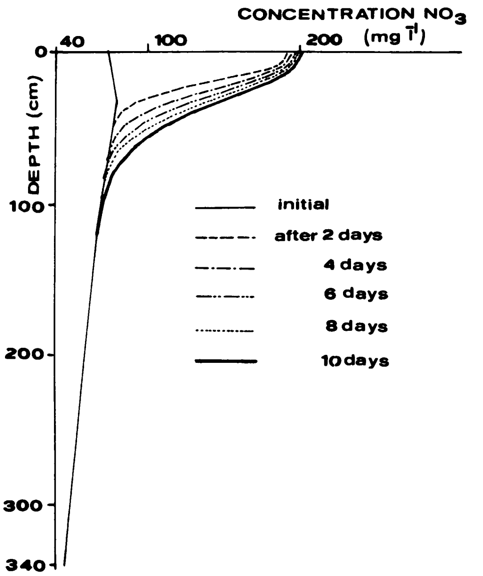

FIGURE 12. Vertical distribution of $N-NO_3^-$ concentrations following application of potassium nitrate with limestone in the nonvegetational season.

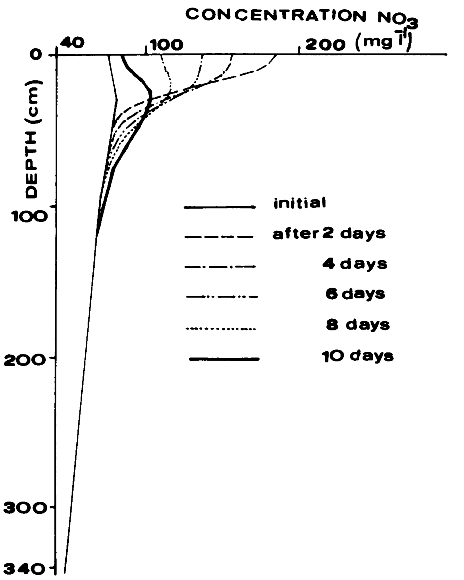

FIGURE 13. Vertical distribution of $N-NO_3^-$ concentrations following application of potassium nitrate with limestone in the vegetational season.

obtained. This, in turn, depends on adequate mathematical description and the actual form in which the individual processes take place *in situ* and the quality and complexity of input data.

Adequate Mathematical Description

Each of the models represents a certain schematic simplification of the processes it describes, and it is the degree of this schematization, the hypotheses, and simplifications adopted, omission of certain influences, etc., that predetermine the quality of model results. The deterministic models are based on the following assumptions:

- The porous medium is assumed to be continuous: Darcy's equation is assumed to hold true; the effect of preferential paths is neglected, etc.
- The transport is considered in the isothermal regime
- Water flow is one-dimensional
- The effect of the solute on water properties such as viscosity, surface tension, and specific mass is neglected
- Porosity, hydraulic conductivity, and other characteristics are constant in time
- Adsorption/desorption is assumed to be a fully reversible process
- The transformation processes are most frequently described by first-order kinetic equations, without taking into account the thermal dependence of these processes, the presence of various other substances, or other factors

Many of these assumptions are very remote from the real-life form in which these processes occur in natural conditions.

Quality and Complexity of Input Data

In regard to quality and complexity of data, two basic problems emerge quite distinctly: representativeness of laboratory input data, and time and spatial variability of input data.

Representativeness of Laboratory Input Data. Parameters of retention curves, unsaturated hydraulic conductivity, dispersivity, and other characteristics are usually measured on intact soil samples. These values may be up to several orders lower than those determined in the field. The main reasons for this consist in the method of collecting the intact soil samples (sampling from a block of compact soil) and in the fact that the samples cannot reveal the different preferential paths of flow. Measurement results also depend on the size of the samples (REV) where, especially for some parameters, the scale effect is manifested.

Time and Spatial Variability of Input Data. The spatial variability of certain types of input data was regarded with special attention at the Nová Ves experimental station. Soil was sampled and some field measurements were carried out in a system of points located on two mutually perpendicular, straight lines. The distance between each two collection/measuring points was 5 m. This situation is schematically depicted in Figure 14.

The purpose of these measurements was to determine the spatial dependence of the parameters observed. Sets of the soil water content values for depths of 5 and 45 m and the semivariograms of these data are plotted in Figure 15.

The semivariograms indicate a certain spatial dependence of the soil water content at a depth of 5 m in samples taken along the A-A line. Analogously, this figure shows the set of the soil water content values

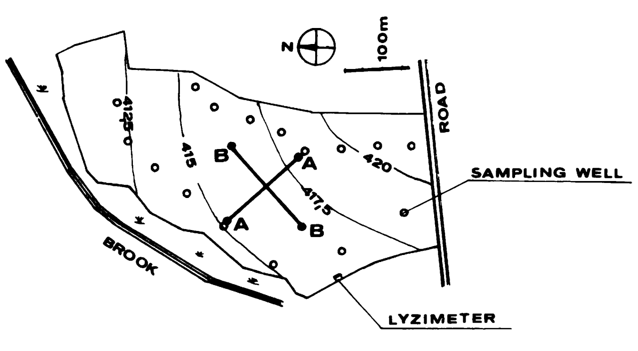

FIGURE 14. Layout of the Nová Ves experimental station.

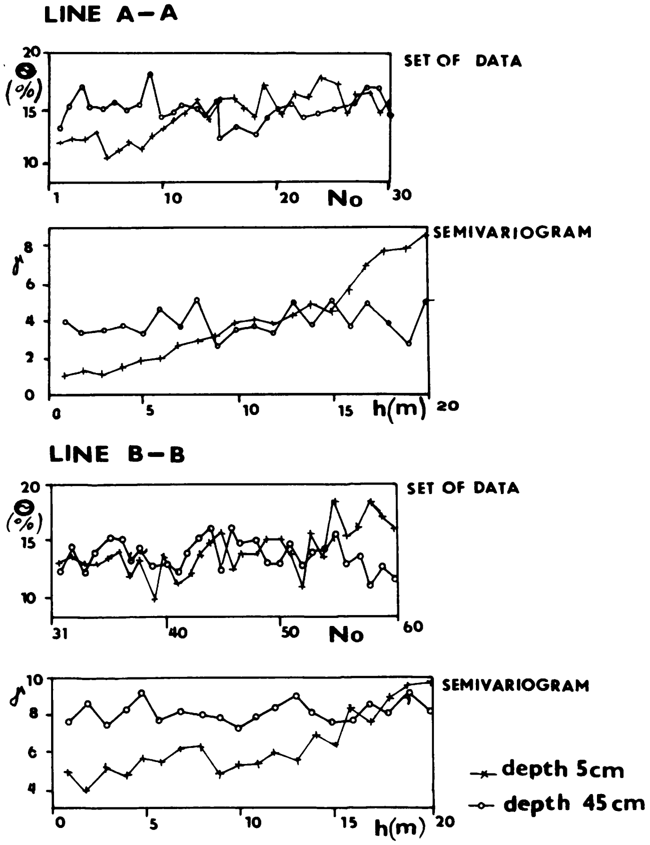

FIGURE 15. Sets of soil water content values and their semivariograms.

measured at points along the B-B line. The corresponding semivariograms suggest a completely random character of these sets. Similar geostatistical analyses were carried out for granularity, $N-NO_3^-$ concentrations, pH, infiltration velocity, and other data.

Apart from the spatial variability, certain input data reveal their variability in time. Not only the initial and boundary conditions of the climatic character vary in time; this variability is also a feature of the parameters that describe the individual transport and transformation processes (retention curves and unsaturated hydraulic conductivity are affected by agrotechnical operations, etc.).

Experiences

The experiences gained from the relatively extensive laboratory and field measurements, as well as model calculations, have yielded some interesting results from which the following conclusions are drawn: *a*) the current types of deterministic transport models are not suitable for long-range prognostic calculations of pollutant transport in the unsaturated zone or groundwater contamination by these pollutants; *b*) these models are suitable for the relative assessment of individual variants of optimizing human activities with a view to groundwater quality protection; *c*) deterministic models require detailed specification of the processes that occur during pollutant transport in the unsaturated zone and selection of an adequate mathematical description of these processes; this aspect is significant in respect to methodology as well as to the development of other types of models (balance, statistical, black-box, etc.) and *d*) deterministic models should be accompanied with a stochastic description of certain parameters, the option to take into account the preferential paths of water flow, transport in the nonisothermal regime, and other aspects, thereby making it possible to employ them in routinely solved problems of groundwater quality protection.

Legislative Aspects of Groundwater Protection

In Czechoslovakia, the legislative aspects of groundwater resources quality protection and conservation are stipulated in the Water Law, which was issued as the Federal Act No. 138/1973. Water legislation in Bohemia has a long tradition. For instance, King Vladislav's Land Constitution of 1500, based on the Roman principle of "*Flumina omnia sunt publica*," states that since ancient times, rivers have been a public commodity. As regards groundwater, it was considered in the past to be "*res omnium communis*" or "*res Nullius*," i.e., belonging to no one, and thus available for ownership by anyone who was legally entitled, above all the respective landowner. Today, the use of groundwater cannot be claimed by virtue of land ownership; it is regulated by state authorities.

The law distinguished three types of water: surface, ground and special, such as mineral, curative, and mine waters. Under this law, groundwater is to be used preferably for drinking purposes. Its resources are subject to obligatory protection, evaluation, and registration. As with the other natural resources, groundwater inventory is undertaken by the State Commission for Classification of Natural Resources.

Protection of groundwater resources is based on the assumption that all of the effectively accessible groundwater is or will be tapped for drinking purposes, and therefore its protection is desirable. The legislation differentiates between overall protection of groundwater resources and comprehensive protection of public water supplies.

Groundwater supply sources are legally safeguarded by protection zones that are delineated in three degrees. Well-head protection, as part of water protection policy and strategy programs, is based on the relevant legislation. Under its regulations, the properties and vulnerability of the hydrogeological system, the kinds and quantities of the existing and potential pollution sources, as well as the pumping rate and the drawdown depth of the water table in wells of the given supply system must be determined and analyzed when the delineation of the groundwater protection zones is undertaken.

First-degree groundwater protection zones shield the well or wellfield and its immediate environment from mechanical damage and direct pollution. Their extent is usually small—several tens of square meters is the maximum. They are excluded from agricultural use and other human activities. Owing to the small extent of the first-degree protection, the costs on land acquisition are negligible.

Second-, and especially third-degree groundwater protection zones are extensive—several hundreds of square meters to several square kilometers, and include the discharge areas, the cones of depression (zone of influence) around pumping wells, the recharge and contribution areas, and the other vulnerable areas of a given water supply system. Second-degree zones comprise areas having a delay or residence time of 50 days, and protect water supply wells against the risk of microbial contamination. The third-degree zones protect groundwater quality in water supply wells from persistent chemical contaminants. This is the most extensive zone, but restrictive measures there are weaker. The recommended residence time is 10 years as the minimum. The second- and third-degree zones cover significant portions of land, often rich in fertile and cultivated soil. For this reason,the delineation of protection zones should involve a complex of up-to-date methods and techniques to minimize the degree of uncertainty in their definition. A sophisticated approach to protection zone delineation should be emphasized.

Within the frame of overall protection of groundwater resources, in the "protected areas of natural water recharge and accumulation," anthropogenic activities are under control and frequently partially restricted by law. These areas cover several hundreds of square kilometers and include the recharge and contribution areas of important groundwater basins.

As concerns agricultural activities and the related potential sources of diffuse pollution, the Ministry of Agriculture and Nutrition, in cooperation with the Ministries of Health and Water Management, issue special regulations on the control over agricultural activity and water resources protection. These regulations are amended every 5 years. There exist no statutory regulations limiting the dosage of the inorganic fertilizers applied. The doses of inorganic nitrate fertilizers are determined with a view to the type of crop and soil and the climatic conditions. The calculated balance also allows for the nitrogen released from organic fertilizers. The guide figures are modified depending on the parameters of the regional or local agro-groundwater systems. When a total dose exceeds 60 kg N/ha/year for the moderately warm regions (average annual temperature of 5 to 9°C) or 80 kg N/ha/year for the very warm regions (average annual temperature higher than 9°C), the fertilizer must be applied in several smaller doses. In Czechoslovak conditions, the recommended total dose of nitrogen per hectare should not be greater than 200 kg/year for arable land. The use of municipal and agricultural effluents for arable land is prohibited in the first- and second-degree protection zones, unless they are composted beforehand.

The use of agricultural effluents is regulated in the following way: first zone, application prohibited; second zone, only composted solid and liquid cattle manure and effluents are allowed; third zone, solid and liquid manure and effluents may be permitted, but their application is under control. The use of pig manure and effluents is not permitted in groundwater protection zones. The doses to be applied are controlled depending on the results of diagnostic analysis of soils and crops. The above recommendations are not yet being sufficiently adhered to, even though they constitute a very progressive element on the sphere of groundwater protection, especially that from nitrate pollution.

The growing number of groundwater pollution episodes in the 1970s prompted the Government to issue three regulations concerning the establishment of a long-term groundwater protection management program and national and regional groundwater quality monitoring networks, with the objective of introducing systematic control over the groundwater resources quality protection and conservation.

A specialized office in charge of control over water quality, the State Water Management Inspection, is in operation in the country. This office imposes various sanctions on the polluters. In exceptional cases, the violation of the Water Law may be prosecuted under criminal law. The extent of the Czechoslovak Water Law and the related regulations is adequate for groundwater resources protection. The principal reasons why the law is not being observed, and the subsequent water contamination occurs, include a low level of responsibility exhibited by certain enterprises, factories, and cooperative farms which handle toxic and harmful materials and the latter's leakages into the water system; shortage of qualified personnel for the preventive control of potential polluters of groundwater resources; and insufficient financial penalization, particulary in cases of extensive contamination of the hydrogeological system.

Health Implications of Nitrates in Groundwater

The Czechoslovak drinking water standards set the maximum content of nitrates at 50 mg/L, for infants at

15 mg/L. An incorrect usage of nitrogen fertilizers leads to increased levels of nitrate concentrations in groundwater and the food chain. It is estimated that the total dietary intake of nitrates in drinking water is less than 30%. Hepatotoxic and carcinogenic nitrosamines are highly hazardous, since they easily penetrate biological membranes. High doses of fertilizers may result in nitrates not being metabolized, with their deposition in plants as ballast. Spinach, carrots, kohlrabi, and beets are especially liable to accumulate nitrogen. There is a close relationship between high nitrate contents in groundwater consumed for drinking and alimentary methemoglobinemia, which can be fatal for infants. (Through bacterial action nitrates are reduced to nitrites that cause the hemoglobin in blood to change into methemoglobin that is unable to transport oxygen.) In Czechoslovakia, it is strongly recommended to use for infants exclusively bottled waters that fully comply with health requirements.

Methemoglobinemia in infancy, under European conditions, appears rarely when privately dug wells with high nitrate contents are used for water supply. According to the WHO, since 1945, some 2000 cases of methemoglobinemia have been reported, with a case fatality of about 8%. Adverse health effects (gastric cancer, birth defects, cardiovascular diseases, effects on the thyroid gland) as a consequence of long-term consumption of water with high nitrate contents are under study in Czechoslovakia. Health risks can also arise when high nitrate contents are combined with pesticides, or when their residuals form carcinogenic nitrosamines.

Adverse effects of agricultural activities on human health project into social and economic spheres (sickness and death rates, migration of population, lower working activity, etc.). In managerial schemes for regional agro-hydrosystems, health risks posed by fertilizers and pesticides should therefore be the subject of continuous monitoring, control, and analysis.

Conclusions

Research into the impact of farming activities on the groundwater quality in experimental fields indicates that a maintained nitrogen and carbon balance is essential for groundwater quality conservation, especially for aquifers overlaid with farmland. The research in experimental fields and the simulation of transport and transformation processes with the help of the WASTEN deterministic model have shown that the processes which occur in the unsaturated zone strongly control the amount of nitrogen leached into the saturated zone.

The regional-scale increase in nitrate contents in shallow aquifers located in the fluvial deposits of the Elbe River, central Bohemia, are decisively affected by farming activities, particularly the high doses of inorganic fertilizer applied. During the past 30 years, nitrate contents in groundwater under cultivated arable land have doubled, as have cereal yields, while the amount of fertilizer applied has grown nearly 8-fold.

Short-term cyclic changes in nitrate content have been identified in the aquifer's upper parts, depending mainly on climatic conditions. The fast response by the shallow aquifer's system to extreme climatic situations is particulary emphasized. The long-term changes and the increasing trend in nitrate concentrations in groundwater reflect anthropogenic, especially farming, influences.

Comprehensive management of the agro-groundwater system based on sound scientific information is strongly recommended for regions with conflicting interests of the agricultural and water sectors.

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