# Annales Agriculturae Fenniae

Maatalouden
tutkimuskeskuksen
aikakauskirja

Journal of the
Agricultural
Research
Centre

Vol. 30,3

# Annales Agriculturae Fenniae

JULKAISIJA — PUBLISHER

Maatalouden tutkimuskeskus
Agricultural Research Centre

Ilmestyy 4 numeroa vuodessa
Issued as 4 numbers a year
ISSN 0570-1538



ALASARJAT — SECTIONS

Agrogeologia et -chimica — Maa ja lannoitus ISSN 0358-139X
Agricultura — Peltoviljely ISSN 0358-1403
Horticultura — Puutarhaviljely ISSN 0358-1411
Phytopathologia — Kasvitaudit ISSN 0358-142X
Animalia nocentia — Tuhoeläimet ISSN 0517-8436
Animalia domestica — Kotieläimet ISSN 0358-1438

JAKELU JA VAIHTO

Maatalouden tutkimuskeskus, Kirjasto, 31600 Jokioinen

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Agricultural Research Centre, Library, SF-31600 Jokioinen

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EDITORIAL

# TO OUR READERS

From the beginning of 1992 **Annales Agriculturae Fenniae** (ISSN 0570-1538), **Journal of Agricultural Science in Finland** (ISSN 0782-4386) and **Finnish Journal of Dairy Science** (ISSN 0367-2387) will be merged. The new scientific journal will be called **Agricultural Science in Finland** (ISSN 0789-600X).

Agricultural Science in Finland will carry original reports on agricultural research, including agricultural economics, agricultural technology, animal science, dairy and food science, environmental science, horticulture and plant and soil science.

The annual volume of Agricultural Science in Finland will average 850 pages, divided in six issues. The current readers of all three journals will not lose out — the amount of information will remain the same. On the contrary, receiving it all in one instead of in three volumes will increase readers' convenience. Readers of one or two of the three currently published journals will, naturally, benefit by receiving more information than before.

The annual subscription will be 500 FIM for others than members of the Scientific Agricultural Society of Finland and the Finnish Society of Dairy Science. Subscriptions can be taken out at bookstores and book agencies. In addition, exchange arrangements may be negotiated.

Manuscripts offered to the journal should be addressed to co-editor Sari Torkko, Agricultural Research Centre of Finland, Data and Information Services, 31600 Jokioinen, Finland. Phone 358-16-188247. Fax 358-16-188339.

We trust that you will welcome the journal merger and enjoy the new journal. We will be pleased to answer your enquiries concerning the new journal.

Sincerely,

*Editor*

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 219—309 (1991)
Seria AGROGEOLOGIA ET -CHIMICA N. 158 — Sarja MAA- JA LANNOITUS n:o 158

# SPLIT APPLICATION OF NITROGEN: EFFECTS ON THE PROTEIN IN SPRING WHEAT AND FATE OF $^{15}$N-LABELLED NITROGEN IN THE SOIL-PLANT SYSTEM

## Selostus: Jaettu typpilannoitus: vaikutukset kevätvehnän valkuaiseen ja $^{15}$N-merkityn lannoitetypen jakautumiseen maassa ja kasveissa

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*Academic dissertation*
*To be presented, with the permission of the Faculty of Agriculture and Forestry of the University of Helsinki, for public criticism in Auditorium XII on March 18th, 1992, at 12 o'clock a.m.*

Vammalan Kirjapaino Oy 1992

# PREFACE

The present study was carried out at the Section of Agricultural Chemistry and Physics of the Institute of Crop and Soil Science, Agricultural Research Centre of Finland, in 1985—1991. I wish to express my sincere gratitude to Professor Paavo Elonen, Head of the Institute of Crop and Soil Science, for suggesting me the subject of this study and for his support over the years.

I am very grateful to my teacher, Professor Antti Jaakkola, Head of the Department of Agricultural Chemistry, University of Helsinki, for his support and guidance at all stages of the work.

My sincere thanks are due also to Professor Paavo Elonen and Professor Hannu Salovaara for checking my work and for their valuable and constructive criticism.

I want to express my grateful appreciation to the staff of the Section of Agricultural Chemistry and Physics for their technical assistance. My warmest thanks are due especially to Mr. Risto Tanni, Mr. Tuomo Nissi and Mr. Kimmo Kakkonen for taking care of the practical aspects of the field experiments, to Miss Mirva Ceder, Miss Jaana Pukkila, Mrs. Leena Seppänen and Miss Erja Äijälä for field work and chemical analyses, and to Mrs. Marjatta Ahola, Mrs. Kerttu Hämäläinen and Mrs. Kirsti Niskanen for technical assistance, as well as Mrs. Rauha Kallio and Mrs. Sinikka Salminen for drawing the figures. My thanks are extended to the staff of the Research Station of Southwest Finland for performing some of the experiments, and especially to the Head of the Research Station, Dr. hc. Jaakko Köylijärvi, for making the principal plans for the large field experiment.

My thanks are extended both to the Head and the staff of the Section of Crop Science, and the Institutes of Environment and Plant Breeding for performing some of the analyses. My special thanks are due to Miss Elisa Pietilä, M.Sc., who was responsible for testing the baking quality, and to Mrs. Sirpa Saarinen, M.Sc. for teaching us the fractioning procedure of the grain proteins.

The English manuscript was linguistically revised by Mrs. Sevastiana Ruusamo, M.A., and edited by Mrs. Sari Torkko, to whom I express my appreciation for their expert work.

I would like to thank the Ministry of Agriculture and Forestry and Kemira Ltd for grants to help me finance my research work.

Finally, I am grateful to the Agricultural Research Centre of Finland for including this study in their series of publications.

Jokioinen, December 1991

*Martti Esala*

# CONTENTS

# SPLIT APPLICATION OF NITROGEN: EFFECTS ON THE PROTEIN IN SPRING WHEAT AND FATE OF $^{15}$N-LABELLED NITROGEN IN THE SOIL-PLANT SYSTEM

ESALA, M. 1991. Split application of nitrogen: effects on the protein in spring wheat and fate of $^{15}$N-labelled nitrogen in the soil-plant system. Ann. Agric. Fenn. 30: 219—309. (Agric. Res. Centre, Inst. Crop Soil Sci., SF-31600 Jokioinen, Finland.)

Abstract. The effect of time of application and the form of nitrogen for top dressing on the yield and quality, especially the protein content and protein baking quality, in spring wheat, and on the fate of $^{15}$N-labelled nitrogen was investigated.

In field experiments on clay soils, the highest yield was obtained by applying the total 140 kg/ha nitrogen at sowing. By splitting 40 kg/ha of this dose at tillering or at ear emergence the yield decreased by 3—5 %. The protein and gluten contents in the grain increased the more the later the application, the highest average increases in protein content being 0.6 percentage units. The falling number, test weight, thousand grain weight, loaf volume or rheological properties of the dough were not affected. Lodging decreased slightly by splitting. Growth regulator treatment increased the yield, but decreased the protein content by 0.3 percentage units. The two varieties of different type did not differ in their reaction to split application of nitrogen.

Urea spraying produced lower protein and gluten contents than calcium ammonium nitrate, calcium nitrate or granular urea. The fertilizers did not differ in their effect on the yield, baking quality or other quality factors.

In a pot experiment, the effect of seven applications of $^{15}$N-labelled fertilizer from sowing to two weeks after ear emergence was compared. The highest recovery was obtained by application at the flag leaf stage.

In field experiments on clay and sandy soils, the recovery of $^{15}$N-labelled nitrogen was highest when applied at ear emergence in a wet summer and when applied at sowing in a summer with dry former part. In other two years the recoveries were not affected by the time of application. The recoveries were 15—25 % in the dry summer and about 60—70 % at their best in summers with ample moisture conditions. The recovery of foliar-applied urea was lower than that of top dressed nitrate nitrogen or ammonium nitrate applied in spring.

The time of application did not clearly affect the amount of $^{15}$N-labelled inorganic nitrogen in the 0—90 cm soil layer at harvest. The recovery of foliar-applied urea nitrogen as inorganic nitrogen was lower, but as organic nitrogen higher than that of nitrate nitrogen top dressed or ammonium nitrogen applied in spring. The inorganic nitrogen consisted of more than 80 % of unlabelled nitrogen. A dry former part of the summer resulted in high amounts of inorganic nitrogen at harvest.

In the pot experiment, the gliadin, glutenin and the residue fractions, but not the albumin + globulin fraction of the grain proteins were increased more the later nitrogen was applied. In the field experiment, no corresponding increases were noticed. The behavior of $^{15}$N-labelled nitrogen did not differ from that of the unlabelled nitrogen with respect to the amount in the protein fractions.

Index words: spring crops, triticum, spring wheat, protein content, protein quality, protein fractions, yield quality, nitrogen fertilizers, timing of application, nitrogen-15, inorganic nitrogen, ammonium nitrate, calcium nitrate, urea

# 1. INTRODUCTION

Nitrogen is the most important plant nutrient affecting the protein content of a crop. It also affects the yield and other quality factors of the grain yield more than any other plant nutrient. Nitrogen fertilizers form a great proportion of the economical input applied to a crop. It is also, besides phosphorus, the most important plant nutrient causing environmental problems.

Wheat grain contains 8—16 % protein, about 70 % starch, 15 % water, and small amounts of other compounds such as lipids and pentosanes (HOSENEY 1986). Four fractions of proteins, i.e. albumins, globulins, gliadins and glutenins, are usually separated by different extraction procedures (PAYNE and RHODES 1982).

The use of wheat flour for bread making is based on its ability to form gluten when mixing flour in water (HOSENEY 1986). Gluten is formed mainly by gliadins and glutenins that are located in the endosperm of the wheat grain. Albumins and globulins are situated in the embryo and in the aleurone layer next to the seed cortical layers, and so they are husked off and transferred to the bran when the grain is milled.

For a wheat of good baking quality two requirements must be met, a protein content of 12—13 % and a high quality of protein (SALOVAARA 1989). The grain must contain enough gluten forming proteins and the ratio of their subunits must be right for good functioning of them during the baking process. The protein content is affected among other things by genetic and environmental characteristics and nitrogen fertilization (MIFLIN and SHEWRY 1981, PAYNE and RHODES 1982). The protein quality is mainly affected by genetic characteristics and probably also partly by weather conditions and fertilization.

Low alpha-amylase activity is an even more important quality factor of bread wheat than protein content and quality. A low Hagberg falling number affected by high alpha-amylase activity is the most important factor decreasing the baking quality of wheat in Finnish conditions (HUTTUNEN 1985).

The protein content of Finnish wheat has gradually diminished from about 15 % in the turn of the 1960s and 1970s (Fig. 1). In some years, average protein content has been less than 12 %, which is not enough for bakeries. The problem has been worst in spring wheat, because winter wheat covers only about 10 % of the wheat area in Finland. In recent years the protein contents have been higher. To raise the protein content the farmer has been paid a premium for the protein content of wheat in Finland since 1989.

The decreasing and year to year variation of the protein content of spring wheat is assumed to be mostly a consequence of variations in weather conditions and yields (KÖYLIJÄRVI 1984). New high yielding, low protein varieties and crop rotation with less grassland leading to less soil nitrogen mineralisation have been considered minor reasons for the diminution of the protein contents of spring wheat in Finland. In fact, the soil nitrogen potential and, to a lesser extent the soil mineralization rate have been noticed to decrease e.g. in Australia, when native grassland soils are cultivated for several years (DALAL and MAYER 1987). This may occur in a smaller scale also in Finland, when crop rotations include less leys.

The most important methods for increasing the protein content and protein quality in wheat for bread making include the breeding of better varieties, addition of vital wheat gluten to wheat flour as well as cultivation techniques.

Breeding of high protein varieties is difficult, because of the genetic interrelationship of high protein content in the grain and low grain yield, but there are some signs of braking this correlation (SVENSSON 1984). The protein content in the official variety tests of the modern Finnish

spring wheat varieties ranged in 1983—1990 from 13.3 to 15.9 % (KÖYLIJÄRVI and TALVITIE 1991).

The baking quality of low protein wheat flour can be improved by adding vital wheat gluten separated from wheat by the starch industry (AITKEN and GEDDES 1938). This has been a practice in many countries, but its benefit has been questioned and it is dependent on the price of gluten flour (MCDERMOTT 1985).

Nitrogen fertilization is the most important cultivation technical means for increasing the protein content of spring wheat. The protein content of the grain increases linearly with increasing fertilizer amount, at least up to the nitrogen dose of 200 kg/ha (e.g. BENZIAN and LANE 1981, SIMAN 1983, ESALA and LARPES 1984a and b). Optimum yield is reached by lower fertilizer doses, and the economical optimum is even lower than the biological optimum. Also lodging of the crops and the resulting lower quality increases, with increasing nitrogen fertilization. The environmental problems caused by nitrogen decreases the possibilities of increasing nitrogen fertilization. This together with the above reasons restrict the possibilities of increasing the protein contents of spring wheat by increasing the nitrogen fertilizer doses. In Finland, the highest recommended fertilizer rates for spring wheat are 130—140 kg/ha.

The protein content of cereals can be increased also by top dressing nitrogen fertilizer during the growing season (e.g. KONTTURI and

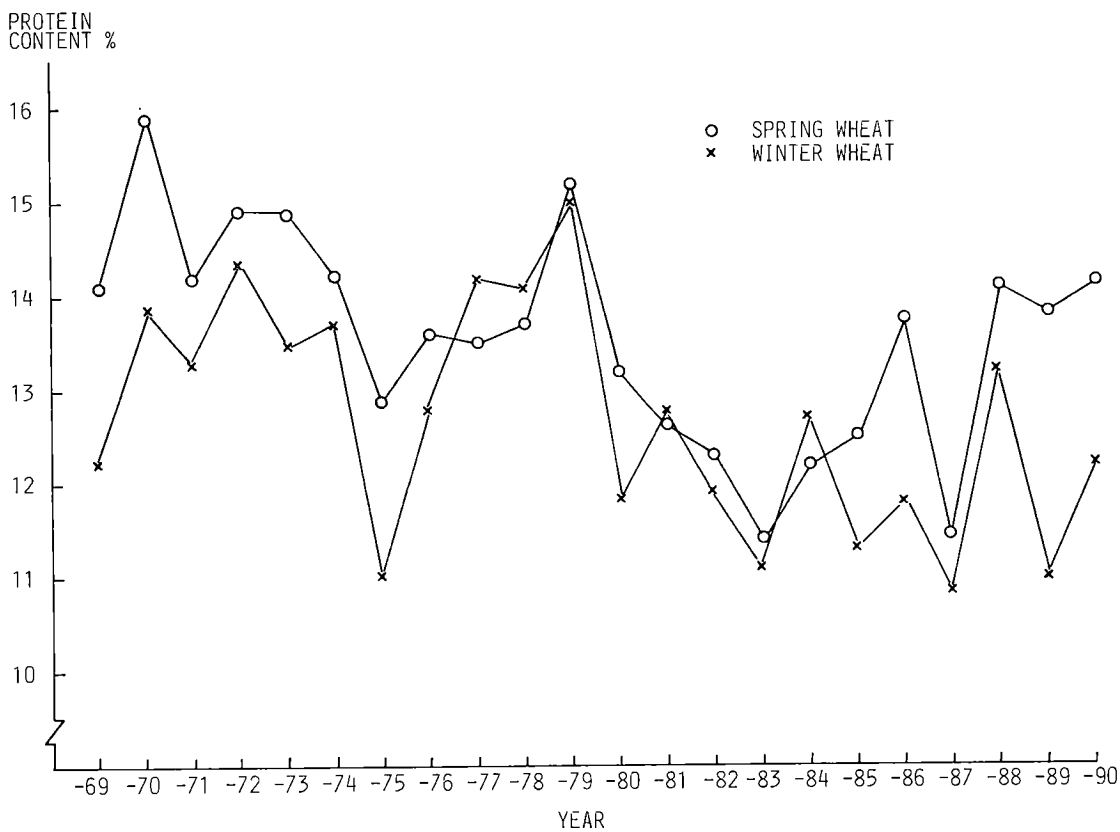



Fig. 1. The average protein contents of wheat in Finland in 1969—1990 according to the Research Laboratory of the Finnish Grain Board (ANON. 1969—90).

RANTANEN 1986, KÖYLIJÄRVI 1987, LAMPINEN 1989). The principle of top dressing is to assure the nitrogen nutrition of the plant also during the grain filling period. This has been notised to increase photosynthesis and the leaf age, which increases yield (NATR 1972, SPIERTZ and ELLEN 1978). Better nitrogen nutrition also increases protein content of the grain. Some contrasting results have been obtained concerning the quality of the protein produced by late application of nitrogen fertilizer. Especially late urea spraying has been noticed in some cases to lower the baking quality of protein (MCNEAL et al. 1963, PUSHMAN and BINGHAM 1976, TIPPLES et al. 1977, DAMPNEY 1987, HEIMONEN-KAUPPI et al. 1987).

The aim of this study was twofold. First, the effect of timing of nitrogen fertilizer application and form of fertilizer nitrogen on the protein content and quality of protein of spring wheat was investigated. The yield and quality factors of the yield other than protein content were taken into account, because these factors affect the value of the yield in the industry as well as the price a farmer is paid for the yield.

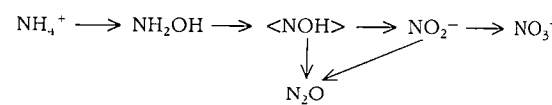
Second, the fate of split applied fertilizer in the soil and plant, and the efficiency of nitrogen fertilization were investigated. The $^{15}N$-technique was used in these investigations.

## 2. THE MOVEMENT OF NITROGEN FROM SOIL TO PLANT AND TO THE PROTEINS OF THE GRAIN, AND THE FUNCTION OF PROTEINS IN THE BAKING PROCESS — A REVIEW

### 2.1. Soil nitrogen

Usually 90—95 % of the nitrogen in the top layer of arable soil is in organic form (WILD 1988). The remaining 5—10 % is in the nitrate or ammonium form, part of the latter fixed in the interlayers of clay mineral lattices. The carbon/nitrogen ratio of the soil organic matter is quite stable, typically 10—14 in the top layer. So, the total nitrogen content of arable soil is greatly dependent on the organic carbon content of the soil.

Nitrogen circulates in the soil, plants and animals in organic and inorganic forms (Fig. 2). The heterotrophic organisms of soil release ammonium nitrogen from the organic matter in the ammonification process (LADD and JACKSON 1982). Ammonium nitrogen is oxidized to nitrate in the biphasic nitrification process as a consequence of the operations of the bacteria mainly of the genera Nitrosomonas and Nitrobacter (NICHOLAS 1978, SCHMIDT 1982):




Also $N_2O$ and $N_2$ can be formed from the intermediates of nitrification process and they are volatilized from soil in gaseous form (BREMNER and BLACKMER 1978). The plants take up nitrogen as ammonium or nitrate. Also the soil microbes take up nitrate and ammonium nitrogen, which are thus returned to the fraction of soil organic nitrogen.

Because nitrate ion is fixed to the soil surfaces only to a minor extent, it is easily movable and easily leacheable (JANSSON and PERSSON 1982). Nitrate can also be denitrified to gaseous $N_2$ or $N_2O$, if the partial pressure of oxygen in soil is decreased. Some bacteria or blue green algae fix atmospheric $N_2$ to forms available to the plants. This process brings more nitrogen to the

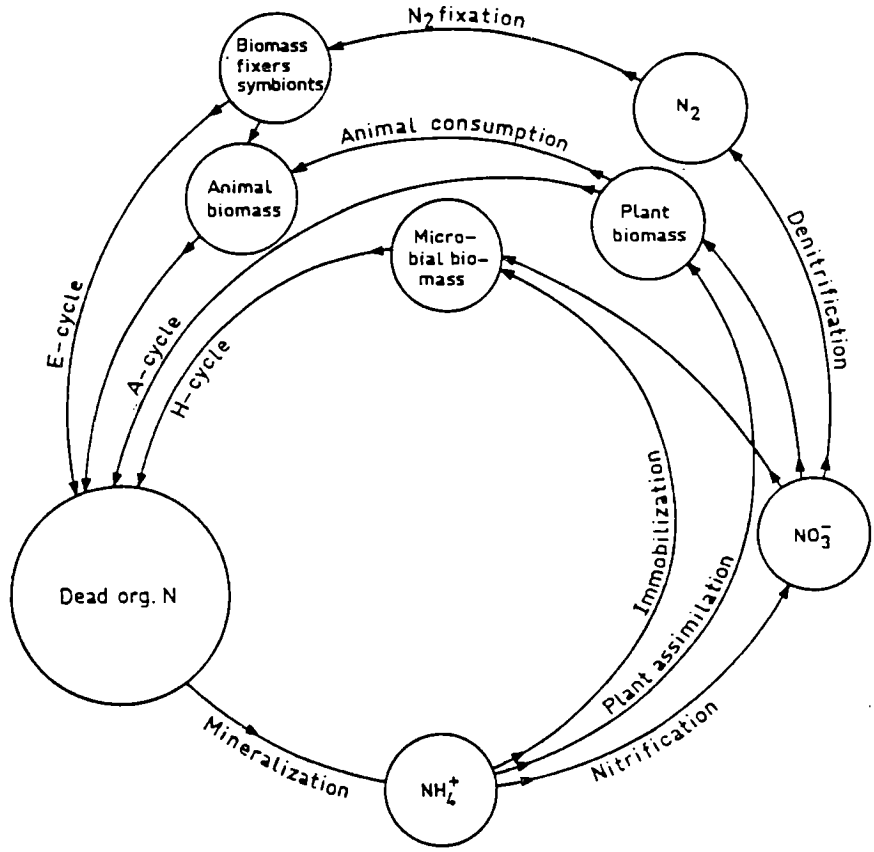



Fig. 2. The universal nitrogen cycle divided into its three subcycles: the elemental (E), the autotrophic (A), and the heterotrophic (H) (JANSSON and PERSSON 1982).

organic nitrogen fraction of the soil after the plant or the microbe has died.

The inorganic nitrogen content of soil fluctuates during the growing season because of the above mentioned mineralization-immobilization turnover, fertilization, plant uptake and losses of nitrogen. Generally, the following kind of fluctuation can be noticed in the inorganic nitrogen content of a certain field in the Scandinavian climatic conditions when spring cereals are cultivated (Fig. 3).

The inorganic nitrogen content of a soil is low in spring because of low mineralization during winter and possibly high leaching losses in spring. Fertilizer application multiplies the amount of inorganic nitrogen. In addition, some nitrogen is mineralized from the soil. During the growing season the content is decreased by the uptake mostly by plants and also soil microbes and by the possible losses through denitrification. By the time the nitrogen uptake by plants has ceased at yellow ripeness the inorganic nitrogen resources of soil are at about the level they were in spring. In autumn the inorganic nitrogen content of soil can be increased by mineralization, because there are no plants to take up the inorganic nitrogen. Leaching and denitrification can, however, remove inorganic nitrogen from the soil.

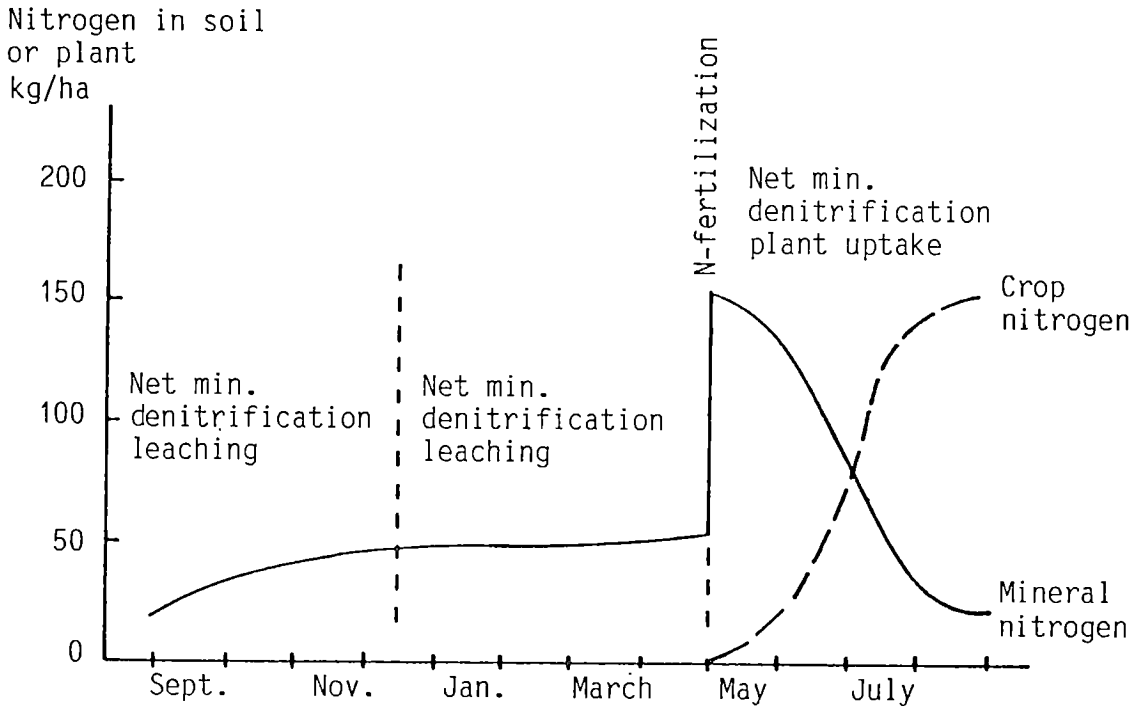



Fig. 3. Changes in the inorganic nitrogen reserves of soil and uptake of nitrogen by the crop in continuous spring cereal cultivation in Central Sweden (according to JANSSON 1983).

## 2.2. Plant uptake and metabolism of nitrogen

The plants take up almost all their nitrogen either as $NO_3^-$ or $NH_4^+$ ions. Ammonium nitrogen is fixed to the soil in cationic form relatively tightly and is less movable than nitrate nitrogen. Ammonium nitrogen is nitrified relatively rapidly. So nitrate is the main form taken up by the plants. The plants can take up also small amounts of nitrogen as nitrite and urea (CRIDDLE et al. 1988).

Nitrate is reduced to ammonium nitrogen in the plant, and further used in the amino acid synthesis. Before being reduced part of the nitrate can be translocated from the roots to the leaves, or it is stored in the roots or the leaves (HUFFAKER and RAINS 1978).

Nitrate is reduced to amino nitrogen in a series of reactions catalysed by the enzymes nitrate reductase (NR), nitrite reductase (NiR), glutamin synthetase (GS), glutamate synthase (GOGAT) and glutamate dehydrogenase (GDH) (Fig. 4) (MIFLIN and LEA 1977, SCHRADER and THOMAS 1981).

The products of these reactions, glutamate and glutamine, are further metabolized to other amino acids such as asparagine, histidine, tryptophane and arginine, as well as nucleic acids, purines and pyrimidines, in reactions catalyzed by aminotransferases (MIFLIN and LEA 1977, 1982, JOY 1988). These aminoacids are further metabolized to other amino acids by aminotransferases.

The nitrogen containing compounds are translocated in the mass flow from the roots to the stems and leaves in the ksylem vessels.

From the location of metabolism, e.g. the leaves, these compounds are translocated to the growing or storing organisms in the phloem.

Asparagine is the most important nitrogen compound translocated. Also glutamine, glutamate and aspartate are included in the ksylem sap (PATE et al. 1965, MIFLIN and LEA 1977). The ratio between the amounts of different amino acids depends to some extent on the source of inorganic nitrogen of the plant. If the ammonium nitrogen content of the cell is increased considerably, asparagine, arginine, and glutamine are formed to a greater extent. Their N/C ratio is favourable for the fast detoxification of ammonia, which is injurious to the cell membranes. Their carbon skeletons are also easily available from the tricarboxyl acid cycle of the plant (IVANKO and INGVERSEN 1971, MIFLIN and LEA 1977, LEA and MIFLIN 1980).

Wheat generally takes up 50—90 % of the nitrogen contained in the grain yield before anthesis depending on the variety and environmental conditions (LAL et al. 1978, LOFFLER et al. 1985, BAUER et al. 1987, VAN SANFORD and MACKOWN 1987). A great part of the nitrogen taken up and reduced before anthesis is stored in the green leaves of the plant as fraction 1 proteins, including mostly enzymes (HUFFAKER 1982). These enzymes function both as catalysts and stores of nitrogen in the leaves.

The most important of the enzymes acting as reserve proteins is ribulose-1,5-bisphosphate-carboxylase-oxygenase (Rubisco) (LEA and MIFLIN 1980, HUFFAKER 1982, MATILE 1982). It catalyzes photosynthetic $CO_2$ assimilation and photorespiration. It constitutes 40—80 % of the soluble proteins in the leaves of e.g. cereal crops. During the senescence the Rubisco enzyme content of the leaves decreases sharply (WITTENBACH 1979, HUFFAKER 1982, LAMATTINA et al. 1985).

Glutamine, asparagine and ammonia are formed in the reactions following the decomposition of the leaf proteins (THOMAS 1978). After decomposition, glutamine and asparagine are translocated in the phloem to the developing grain (LEA and MIFLIN 1980). The ammonia released from asparagine has been noticed to be reassimilated in peas by glutamine synthetase (IRELAND and JOY 1981). ABROL et al. (1983)

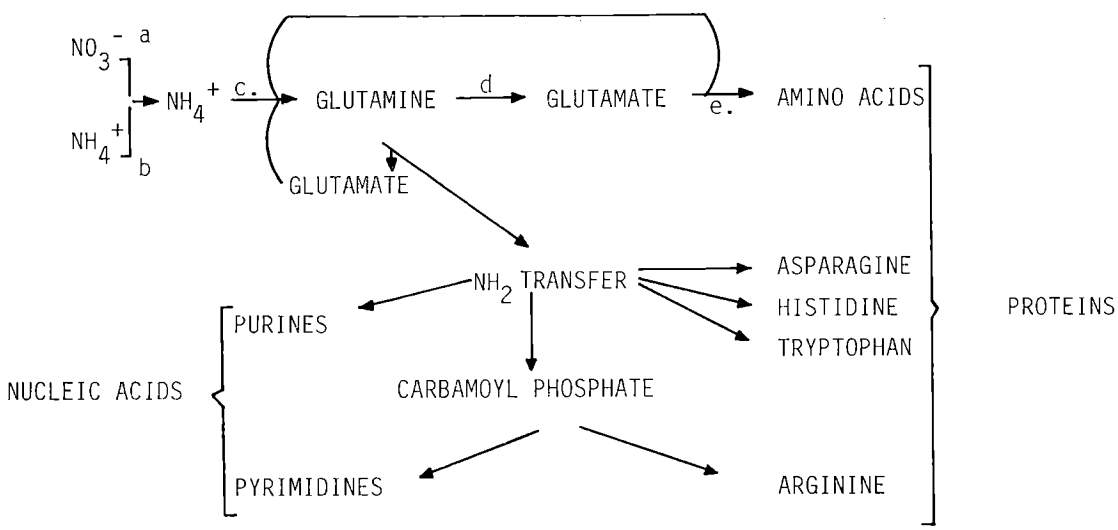



Fig. 4. The metabolism of nitrogen to proteins and nucleic acids via glutamine and glutamate. Enzymes: a.) nitrate reductase, nitrite reductase, b.) ammonium uptake, c.) glutamine synthetase, d.) glutamate synthase, e.) aminotransferases (according to MIFLIN and LEA 1977).

suggested that considerable amounts of ammonia can be volatilized from the leaves in this phase, but other papers on nitrogen metabolism in plants do not discuss this possibility (e.g. LEA and MIFLIN 1980, YAMAYA and OAKS 1987).

## 2.3. Accumulation of proteins in the grain

Cortical layers, endosperm and embryo can be distinguished in the wheat grain (HOSENEY 1986). The cortical layers and embryo are husked off when the grain is milled. Also the outer layer of the endosperm, the aleuron layer, is removed when the grain is milled. The endosperm is formed mainly by starch granules and a protein matrix, which is formed when the protein bodies are packed together by the ripening of the grain. Other compounds of the grain important in the baking process are the hemicelluloses, which are elements of the cell walls, as well as the lipids.

Grain proteins are usually fractionated according to their solubility to different kinds of extractants (Fig. 5). The fractionation was originally developed by OSBORNE (1907, ref. PAYNE and RHODES 1982):

1.) Albumins, extracted by water
2.) Globulins, extracted by salt solutions, but not by water
3.) Prolamins, extracted by alcohol solutions and water
4.) Glutelins, extracted by dilute acids and bases

BUSHUK (1985) distinguishes also acetic acid insoluble fraction as fraction of its own, termed insoluble glutenin.

The prolamins of wheat are termed gliadins and the glutelins are termed glutenins (PAYNE and RHODES 1982). The gluten of wheat is formed by the gliadins and glutenins.

The albumins and globulins are biologically active proteins, e.g. enzymes (MÜNTZ 1982, PAYNE and RHODES 1982). They are located mainly in the embryo and the aleurone layer of the wheat grain, and they are husked off by milling. They are nutritionally more valuable than the gluten proteins, e.g. their lysine content is higher.

The gliadins and glutenins are reserve proteins of the grain, and they are located in the endosperm (MÜNTZ 1982, PAYNE and RHODES 1982, HOSENEY 1986). They are valuable proteins in the baking process, but their nutritional value is less than that of the albumins and globulins.

Four polypeptide groups of gliadins, alfa-, beta-, gamma- and omega-gliadins, can be separated by electrophoresis. Using two-dimensional electrophoresis, the gliadin fraction has been noticed to be formed by about 45 subunits (PAYNE 1987).

The glutenins can be divided into low molecular weight (LMW) and high molecular weight (HMW) glutenins (PAYNE 1987). Also the glutenins are formed of subunits that are held together by the disulphide bonds of cystine. MIFLIN and SHEWRY (1981) consider that actually the glutenins are prolamins which have not been extracted in the previous fraction because of defects in the extraction technique. Using two dimensional electrophoresis, 19 subunits can be separated from the glutenins (WALL 1979, PAYNE 1987).

The absolute amount of albumins and globulins has generally been shown to be relatively stable (DONOVAN et al. 1977) or to increase slightly (GRAHAM et al. 1963, JENNINGS and MORTON 1963, KACZKOWSKI et al. 1986) during the grain development period. SKERRIT et al. (1988)

and TRIBOI et al. (1990) showed that gliadins appeared later at the beginning of grain development than glutenins. According to TRIBOI et al. (1990) the increase of glutenins was rapid at the later grain ripening stages. So, the gliadin/glutenin ratio decreased rapidly at these stages.

## 2.4. Function of proteins in the baking process

The baking process can be divided into three phases: 1.) mixing and development of the dough, 2.) aeration of the dough and 3.) oven-baking of the dough (WALL 1979, PAYNE and RHODES 1982, HOSENEY 1986).

The gluten proteins are hydrated gradually, when the mixture of flour, water and other constituents of the dough is mixed. During mixing the gluten proteins become more soluble, as the disulphide bonds are broken. Dur-

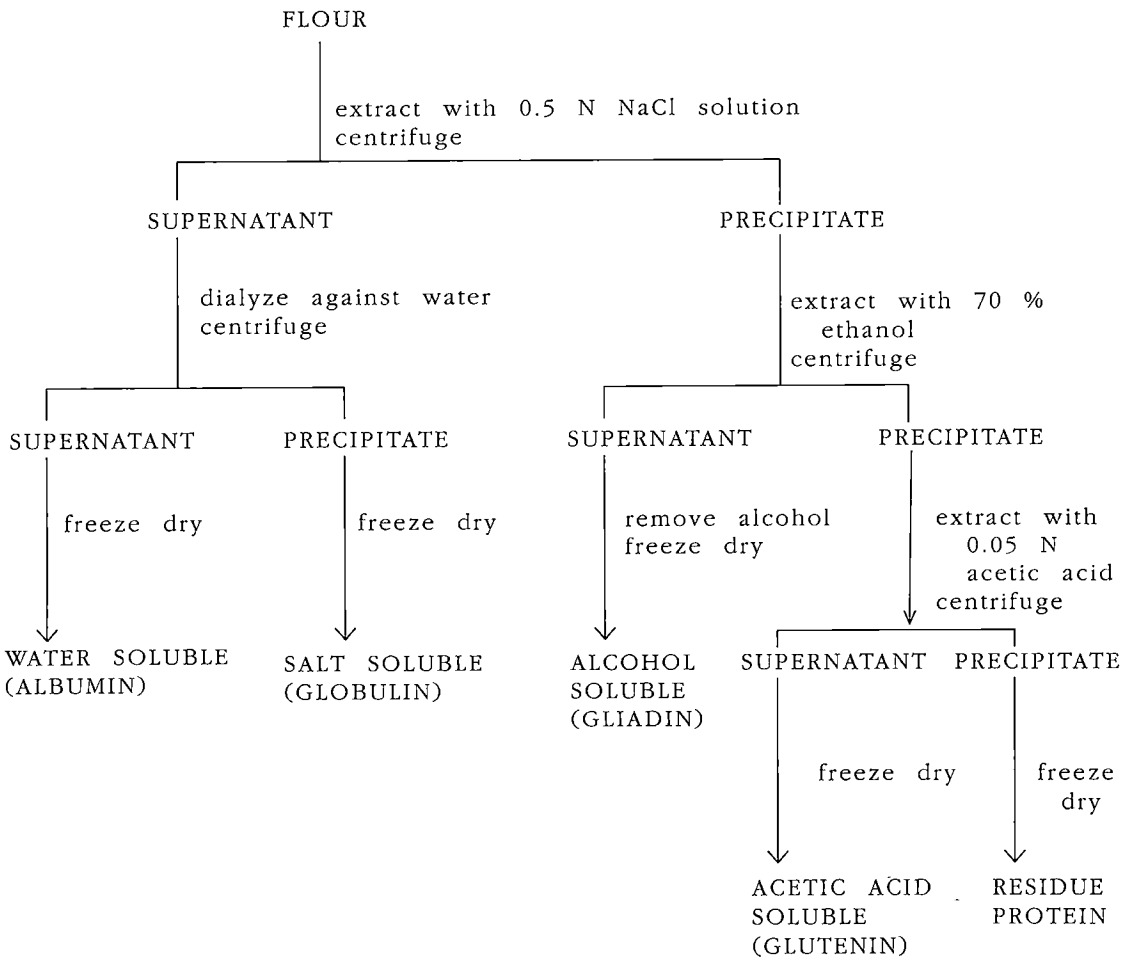



Fig. 5. Modified Osborne fractionation of wheat proteins on the basis of solubility in various solvents (According to BUSHUK 1985).

ing the following rest period the disulphide bonds are reformed and a continuous gluten matrix is formed in the dough under the influence of these bonds as well as the hydrogen and hydrophobic bonds. This matrix retains the $CO_2$ released from the carbohydrates of the flour, and the dough is leavened.

When the dough is oven-baked, the gluten and the starch are coagulated, and the structure of the bread is thus formed.

Generally, all the gluten proteins influence the baking result. The gliadins have only seldom been noticed to correlate with the differences in the baking quality between varieties (HOSENEY et al. 1969, WRIGLEY 1980, DOEKES and WENNEKES 1982), but HOSENEY et al. (1969) noticed that the gliadins affect the loaf volume and the glutenins affect the dough strength.

Several investigations have shown that the acid insoluble residual protein and the high molecular weight glutenins are positively correlated with the mixing properties of the dough (e.g. HOSENEY et al. 1969, ORTH et al. 1972, WALL 1979, MIFLIN et al. 1983).

ORTH and BUSHUK (1972) showed a negative correlation between the acetic acid insoluble glutenin and loaf volume. ORTH et al. (1972), however, showed a positive correlation between residual protein and the loaf volume. The subunits of the residual protein were not shown alone to affect the loaf volume (ORTH and BUSHUK 1973). The albumins and the globulins have not generally been noticed to correlate with the baking quality of the flour in any of the investigations made on the subject (ORTH and BUSHUK 1972, WALL 1979, MIFLIN et al. 1983).

PAYNE et al. (1987) observed a clear correlation between the subunits of the HMW glutenins and the baking quality of a wheat variety. They developed a system for the evaluation of the varieties according to the subunit construction of a variety. The Finnish wheat varieties are in this respect almost equal to the Canadian varieties that are generally well known for their good baking quality (SONTAG et al. 1986, LUKOW et al. 1989).

The reviews of the value of the protein fractions on the baking quality of the flour conclude generally that the dough should contain both gliadins and glutenins in an optimal ratio (e.g. WALL 1979, BUSHUK 1985). This makes the formation of a good, membranous gluten possible, which can retain the $CO_2$ formed during the fermentation of the dough until the firm structure of the bread is formed, as the proteins are thermally denatured when oven-baking the dough.

## 3. MATERIAL AND METHODS

### 3.1. Experiments

The following field and pot experiments were conducted:

1. Split application of nitrogen fertilizer to spring wheat — a field experiment at Jokioinen and at Mietoinen in 1986—1989.
2. The effect of time of application on the fate of $^{15}N$-labelled fertilizer in spring wheat — a pot experiment in 1985.
3. The effect of time of application and form of nitrogen on the fate of $^{15}N$-labelled fertilizer in the soil-plant system a field experiment in 1987—1990

### 3.1.1. Split application of nitrogen fertilizer to spring wheat — a field experiment

*Experimental design*

Three commercial nitrogen fertilizers, i.e. calcium ammonium nitrate (CAN), calcium nitrate (CN) and urea, were compared in a field experiment by granular top dressing applied to spring wheat. Urea was also applied foliar. The experiment included two varieties and two times of fertilizer application: tillering (growth stage 21) (ZADOKS et al. 1974) and ear emergence (GS 50). These treatments were compared with single application of nitrogen in spring. Increasing the protein content and protein quality in spring wheat was the main aim of the experiment, but also the yield and some other quality factors were considered.

The experimental method was split-plot. The treatment on the main plot was variety, fertilizer on the subplots and time of application on the subsubplots. The basic nitrogen application was 100 kg/ha for all the treatments. The experiments included three control N treatments applied in spring: 100 kg/ha, 140 kg/ha and 140 kg/ha plus growth regulator. A zero N treatment was included in the experiments in 1988—1989. There were four replicates in the experiments. The experimental design was as follows:

FACTORS

A. Variety
   $A_1$ = Heta (in 1986 Luja)
   $A_2$ = Kadett
B. Nitrogen fertilizer used for top dressing
   $B_1$ = 100 kg/ha N as CAN in spring + 40 kg/ha N as CAN granular
   $B_2$ = 100 kg/ha N as CAN in spring + 40 kg/ha N as CN granular
   $B_3$ = 100 kg/ha N as CAN in spring + 40 kg/ha N as urea granular
   $B_4$ = 100 kg/ha N as CAN in spring + 40 kg/ha N as urea sprayed
C. Time of application of top dressing
   $C_1$ = beginning of tillering (GS 21)
   $C_2$ = beginning of ear emergence (GS 50)

CONTROLS

   $D_0$ = no nitrogen (in 1988—1989)
   $D_1$ = 100 kg/ha N as CAN in spring
   $D_2$ = 140 kg/ha N as CAN in spring
   $D_3$ = 140 kg/ha N as CAN in spring + growth regulator

The two varieties were of opposite types: Heta (Luja in 1986) was an early ripening, lower yielding type of higher protein content. Kadett was a later ripening, higher yielding type of lower protein content.

*Soil*

The experiments were situated at Jokioinen (60° 49'N, 23° 30'E) and at Mietoinen (60° 38'N, 21° 52'E) in South-Western Finland. At Jokioinen the experiment was located on the same site in 1986, 1987 and 1989 (experiment 1), but the location was changed for 1988 (experiment 2). At Mietoinen the location of the experiment was changed each year (experiments 3 to 6).

If the location of the experiment was changed from the previous year, the soil was sampled before spring operations to the depths of 0—25 cm and 25—60 cm. Ten subsamples were taken from the topsoil (20 in 1988—1989) and six subsamples from the deeper layer. The subsamples were bulked, the soil was homogenized, and a subsample was taken for soil analysis. The samples were dried in 35 °C.

The experiments were established on clay soils. The pH, extractable nutrients (VUORINEN and MÄKITIE 1955), soil texture (ELONEN 1971) as well as organic carbon (SIPPOLA 1982) and total nitrogen (ANON. 1986) contents are presented in Table 1.

*Field operations*

The experiments were fertilized before sowing with 500 kg/ha of ammonium PK fertilizer (40 kg/ha P, 62 kg/ha K) driving across the plots.

Table 1. Soil properties at the beginning of the experiment.

| | Jokioinen | | Mietoinen | | | |
|---|---|---|---|---|---|---|
| | Exp 1 | Exp 2 | Exp 3 | Exp 4 | Exp 5 | Exp 6 |
| 0—25 cm | | | | | | |
| pH | 6.73 | 6.25 | 6.63 | 6.35 | 6.10 | 6.20 |
| Ca mg/l | 3035 | 2313 | 2620 | 1936 | 1587 | 1553 |
| K » | 341 | 210 | 335 | 280 | 218 | 211 |
| Mg » | 435 | 398 | 782 | 530 | 353 | 272 |
| P » | 37.5 | 16.0 | 7.1 | 10.2 | 10.6 | 18.7 |
| Organic C % | 2.70 | 2.72 | 2.30 | 2.02 | 1.71 | 1.97 |
| Total N % | 0.19 | 0.21 | 0.22 | 0.19 | 0.18 | 0.17 |
| Particle size composition % | | | | | | |
| <0.002 mm | 44.0 | 43.7 | 73.9 | 67.0 | 40.6 | 23.7 |
| 0.002—0.02 mm | 26.5 | 30.5 | 19.6 | 23.2 | 19.7 | 16.1 |
| 0.02—0.2 mm | 21.5 | 19.3 | 5.4 | 8.4 | 33.4 | 49.1 |
| 0.2—2 mm | 8.0 | 6.5 | 1.1 | 1.4 | 6.3 | 11.1 |
| Soil type | clay loam | clay loam | heavy clay | heavy clay | sandy clay | fine sand |
| 25—60 cm | | | | | | |
| pH | 6.69 | 7.75 | 6.87 | 7.10 | 6.60 | 6.80 |
| Ca mg/l | 2673 | 2515 | 1826 | 1599 | 1536 | 1546 |
| K » | 240 | 229 | 309 | 256 | 292 | 278 |
| Mg » | 1129 | 1297 | 1063 | 803 | 858 | 675 |
| P » | 2.2 | 0.6 | 1.2 | 1.7 | 2.0 | 3.6 |
| Organic C % | 1.01 | 0.53 | 1.04 | 0.78 | 0.89 | 0.72 |
| Total N % | 0.06 | 0.04 | 0.08 | 0.06 | 0.08 | 0.09 |
| Particle size composition % | | | | | | |
| <0.002 mm | 55.3 | 61.2 | 77.5 | 74.1 | 70.1 | 44.3 |
| 0.002—0.02 mm | 24.3 | 24.6 | 20.4 | 22.6 | 19.4 | 24.2 |
| 0.02—0.2 mm | 17.9 | 13.1 | 2.1 | 3.3 | 9.1 | 30.3 |
| 0.2—2 mm | 2.5 | 1.1 | — | — | 1.4 | 1.2 |
| Soil type | clay loam | heavy clay | heavy clay | heavy clay | heavy clay | sandy clay |

This amount gave 10 kg/ha of nitrogen, which amount was reduced from the actual treatments applied by combine drilling. So, also the zero N treatment actually received this amount of N. In 1989, only P, no K, was applied 30 kg/ha as triple superphosphate. So the zero N plot received no fertilizer N. The spring application of nitrogen was applied as calcium ammonium nitrate by combine drilling according to the experimental design.

The granular fertilizers used for top dressing were broadcasted using an Öyjord fertilizer spreader (manufactured by Kesko Oy, Finland). At Jokioinen in 1988—1989, a specially designed fertilizer spreader was used, which was based on the principle of an ordinary fertilizer drill (manufactured by Tume Oy, Finland). Urea was sprayed using Azo Propane sprayer supplied with swirl nozzles and designed for experimental purposes (supplied by Azo Sprayers, Holland). The solution was made dissolving 86 kg/ha of urea in 400 l/ha of water.

For the growth regulator treatment, chlormequat chloride (Korrenvahvistaja CCC 0.7 l/ha) was sprayed at the beginning of the stem elongation stage (GS 30). At Jokioinen in 1987, etephone (Cerone 0.8 l/ha) was used for the purpose at the flag leaf stage (GS 47).

At Jokioinen the experimental plots were 2.5 m × 13 m = 32.5 m$^2$, and the harvested plots 1.5 m × 13 m = 19.5 m$^2$ (1.9 m × 13 m = 24.7 m$^2$ in 1987). At Mietoinen the experimental plots were 2.5 m × 11.0 m = 27.5 m$^2$ and the harvested plots 1.5 m × 11.0 m = 16.5 m$^2$.

Table 2. The treatments applied in the experiments.

| Treatment | 1986 | 1987 | 1988 | 1989 |
|---|---|---|---|---|
| | | Jokioinen | | |
| Sowing | 23/5 | 25/5 | 12/5 | 17/5 |
| Fertilizer application at tillering | 18/6 | 24/6 | 6/6 | 17/6 |
| Growth regulator spraying | 26/6 | 8/7 | 15/6 | 21/6 |
| Fertilizer application at ear emergence | 9/7 | 16/7 | 28/6 | 3/7 |
| Harvest, Heta (Luja) | 2/9 | 6/10 | 6/8 | 22/8 |
| Kadett | 5/9 | 10/10 | 12/8 | 30/8 |
| | | Mietoinen | | |
| Sowing | 21/5 | 30/5 | 12/5 | 9/5 |
| Fertilizer application at tillering | 16/6 | 25/6 | 13/6 | 5/6 |
| Growth regulator spraying | 21/6 | 3/7 | 20/6 | 19/6 |
| Fertilizer application at ear emergence | 7/7 | 20/7 | 29/6 | 29/6 |
| Harvest, Heta (Luja) | 29/8 | 12/10 | 11/8 | 22/8 |
| Kadett | 10/9 | 22/10 | 19/8 | 28/8 |

Lodging was observed on each plot before harvesting. The other operations were made according to routine cultivation techniques (Table 2).

### 3.1.2. The effect of time of application on the fate of $^{15}N$-labelled fertilizer in spring wheat — a pot experiment

*Experimental design*

A pot experiment was made in 1985 to investigate the effect of the time of application of nitrogen on the fate of $^{15}N$-labelled fertilizer in the soil-plant system. The experimental design was as follows:

A. VARIETY
- $A_1$ Luja
- $A_2$ Kadett

B. TIME OF APPLICATION OF LABELLED FERTILIZER

| | Growth stage (ZADOKS et al. 1974) |
|---|---|
| $B_1$ No nitrogen top dressing | — |
| $B_2$ Sowing | 00 |
| $B_3$ Beginning of tillering | 21 |
| $B_4$ Beginning of stem elongation | 30 |
| $B_5$ 2-node stage | 32 |
| $B_6$ Flag leaf stage | 47 |
| $B_7$ Ear emergence | 50 |
| $B_8$ Two weeks after ear emergence | 71 |

*Soil*

The soil was taken from the field at Jokioinen in spring. The soil type was fine sand (18.2 % clay, 7.4 % silt, 46.6 % fine sand 27.8 % sand, $pH_{water}$ 6.30, Ca 1715 mg/l, K 116 mg/l, P 21.0 mg/l, Mg 170 mg/l, organic C 1.16 %, total N 0.087 %). The soil was sieved through a 14 mm sieve and homogenized. The volume of the experimental pots was six liters and 6.0 kg field moist soil was weighed in each pot.

*Treatments*

The basic fertilization consisted of 1000 mg N ($NH_4NO_3$), 400 mg P, 1010 mg K ($K_2HPO_4$), 100 mg Mg and 130 mg S ($MgSO_4$) per pot. For top dressing 517 mg nitrogen was applied as $^{15}NH_4{}^{15}NO_3$ (10.3036 atom % excess) in 10 ml of solution. After pipetting the fertilizer, 50 ml of water was added to bring the fertilizer to the root zone. The water that had drained through the soil was returned to the pot after each watering. The variety Luja was sprayed with

triadimephone (Bayleton 25, 1.2 g/l) on 5 July to control mildew (*Erysiphne graminis*). The pots were kept outdoors under a glass shelter.

*Harvesting*

The plants were cut about 2 cm above soil surface. The plants were divided into the following parts: ear, highest internode, second highest internode, lowest (3rd and 4th) internodes. The ears were threshed in an ear thresher, and the chaff including the glumes and the rachis was treated as one sample. The soil was weighed, its dry matter content was determined (105 °C, overnight), and a subsample, from which the roots were picked off, was taken. The roots were separated by washing from the rest of the soil using sodiumhexametaphosphate (2 %, w/v) to disperse the soil. The roots were dried, and roots picked from the subsample of the soil were pooled with these.

### 3.1.3. The effect of time of application and the form of nitrogen on the fate of $^{15}N$-labelled fertilizer in the soil-plant system — a field experiment

*Experimental design and soil type*

A field experiment was arranged in 1987—1990 to investigate the effect of time of application and the form of nitrogen on the fate of $^{15}N$-labelled fertilizer. The experiment was located at Jokioinen. The experimental design was randomized blocks. The plots were $2 \times 2.5$ m microplots ($2 \times 3$ m in 1989). The spring wheat variety was Kadett. The soil was silty clay overlying heavy clay (Table 3). The experimental design for 1987—1988 was as follows:

Nitrogen application kg/ha (* = $^{15}N$-labelled)

| Treatment indication | Sowing (GS 00) | Beginning of tillering (GS 21) | Ear emergence (GS 50) | Form of $^{15}N$-labelled fertilizer |
|---|---|---|---|---|
| A | 0 | 0 | 0 | |
| B | 100 | 0 | 0 | |
| C | 100 + 40* | 0 | 0 | $NH_4NO_3$ |
| D | 100 | 40* | 0 | $NO_3^-$ |
| E | 100 | 0 | 40* | $NO_3^-$ |
| F | 100 | 20* | 20 | $NO_3^-$ |
| G | 100 | 20 | 20* | $NO_3^-$ |

For 1989—1990 the design was as follows:

Nitrogen application kg/ha (* = $^{15}N$-labelled)

| Treatment indication | Sowing (GS 00) | Beginning of tillering (GS 21) | Ear emergence (GS 50) | Form of $^{15}N$-labelled fertilizer |
|---|---|---|---|---|
| A | 0 | 0 | 0 | |
| B | 100 | 0 | 0 | |
| C | 100 + 40* | 0 | 0 | $NH_4NO_3$ |
| D | 100 | 40* | 0 | $NO_3^-$ |
| E | 100 | 0 | 40* | $NO_3^-$ |
| F | 100 | 40* | 0 | Urea |
| G | 100 | 0 | 40* | Urea |

Table 3. Soil properties of the $^{15}N$ field experiment in spring.

| | 1987 | | 1988/89 | | 1990 | |
|---|---|---|---|---|---|---|
| | 0—25 | 25—60 | 0—25 | 25—60 | 0—25 | 25—60 |
| pH | 6.15 | 6.45 | 6.30 | 6.70 | 6.70 | 7.05 |
| Ca mg/l | 2343 | 2474 | 2339 | 2458 | 3071 | 2723 |
| K » | 316 | 287 | 236 | 236 | 263 | 241 |
| Mg » | 575 | 1304 | 364 | 1343 | 287 | 898 |
| P » | 14.2 | 1.4 | 18.9 | 0.8 | 82.0 | 3.8 |
| Organic C % | 2.69 | 0.65 | 2.87 | 0.56 | 2.65 | 0.73 |
| Total N % | 0.218 | 0.086 | 0.272 | 0.042 | 0.202 | 0.070 |
| $NO_3$-N kg/ha | 4.2 | 2.7 | 3.5/9.5 | 3.4/6.8 | 11.8 | 9.4 |
| $NH_4$-N » | 11.5 | 10.6 | 6.0/10.1 | 2.8/3.9 | 8.1 | 4.0 |
| Particle size composition % | | | | | | |
| <0.002 mm | 59.3 | 72.7 | 42.9 | 64.1 | 27.3 | 48.5 |
| 0.002—0.02 mm | 23.2 | 17.5 | 26.3 | 23.5 | 21.4 | 21.0 |
| 0.02—0.2 mm | 13.6 | 8.2 | 23.6 | 11.2 | 44.5 | 28.1 |
| 0.2—2 mm | 3.9 | 1.6 | 7.2 | 1.2 | 6.8 | 2.4 |
| Soil type | silty clay | heavy clay | clay loam | heavy clay | fine sand | sandy clay |

*Treatments*

The experimental treatments are presented in Table 4. Superphosphate 230 kg/ha and potassium chloride 40 kg/ha (20 kg/ha P, 20 kg/ha K) were placed before sowing of the experiment in 1987—1988: In 1989—1990, no K was applied and 30 kg/ha of P was applied as triple superphosphate. The plots, except zero plots, were applied 100 kg/ha of nitrogen by combine drilling 364 kg/ha of calcium ammonium nitrate.

Spring application of $^{15}N$-labelled fertilizer was given as $^{15}NH_4{}^{15}NO_3$ (ca. 5 atom % excess in 1987—1989 and 10 atom % excess in 1990). The top dressing was applied as 75 atom % $K^{15}NO_3$ mixed with $Ca(NO_3)_2 \times 4H_2O$ to achieve 5 atom % excess (10 % in 1990). The enrichment of urea was ca. 4 atom %.

If $KNO_3$ only had been used for top dressing of N, the K amount applied would have been 110 kg/ha, which would probably have affected the results. Calcium was assumed to affect the results less, because its concentration in soil solution is naturally higher than that of potassium. Dilution of the enrichment with calcium nitrate instead of potassium nitrate gave 7 kg/ha of potassium (11.6 kg in 1990) and 50 kg/ha of calcium (38 kg in 1990).

The $^{15}N$-labelled fertilizers were pipetted after sowing of the plots (Finnpipette, supplied by Labsystems Oy, Finland). In spring this was done by opening the fertilizer rows and pipet-

Table 4. Experimental treatments in the $^{15}N$ field experiment.

| Treatment | 1987 | 1988 | 1989 | 1990 |
|---|---|---|---|---|
| Soil sampling in spring | 20/5 | 12/5 | 17/4 | 3/5 |
| Sowing | 26/5 | 14/5 | 12/5 | 14/5 |
| N application at tillering | 25/6 | 8/6 | 12/6 | 13/6 |
| N application at ear emergence | 16/7 | 30/6 | 29/6 | 4/7 |
| Sampling at anthesis | 29/7 | 5/7 | 6/7 | 16/7 |
| Harvesting | 8/10 | 11/8 | 25/8 | 4/9 |
| Soil sampling in autumn | 15/10 | 18/8 | 30/8 | 5/9 |

ting 5 ml of liquid containing the desired amount of fertilizer (231.146 g $^{15}NH_4{}^{15}NO_3$/ 4.04 l water) in each 10 cm of the furrow. The liquid was sampled for determination of the exact $^{15}N$ enrichment of the fertilizer. The furrow was then recovered with the same soil. The method did not affect the germination of the seed, except in 1989 when the soil was crusted by heavy showers after sowing.

The top dressing of $^{15}N$-labelled fertilizer was done by dividing the plot into small squares of 12.5 × 20 cm using a string that was stretched on a wooden frame (Fig. 6). 5 ml of liquid containing the fertilizer was pipetted in each one of these small squares. Each plot received 1000 ml of liquid corresponding to a precipitation of 0.2 mm. Special care was taken not to pipette the fertilizer on the leaves of the crop. In 1989 and 1990, the plots were watered with one liter of water to wash away the possible deposits of fertilizer from the surface of the leaves. Wooden bridges were used when pipetting the fertilizer to avoid trampling on and around the plots.

Urea was sprayed on the crops by the Azo propane sprayer using 400 l/ha of water. All the nozzles were tested to give equal amounts of liquid and special care was taken for the speed of spraying to be right.

*Sampling and harvesting*

A crop sample of 1 m × 0.5 m was taken at anthesis (GS 64) from a distance of 0.3 m from the end of each plot. This sample was dried at 65 °C for the determination of N and $^{15}N$. At harvest, a square of 1 m × 1 m was cut about 2 cm above the soil surface. This left a 0.5 m discard area around the harvested area. The samples were dried (65 °C), threshed, weighed and ground for determination of $^{15}N$. The chaff and straw were bulked. In 1989—1990, the chaff including the glumes and rachis was treated separately, but the results were pooled with the results of straw. In 1989, there was plenty of weeds, red dead-nettle (*Lamium purpureum* L.), on the plots. They were harvested and analysed separately. In all phases the expected low enrichment samples were treated first, and the tools were cleaned thoroughly between the samples to avoid $^{15}N$ cross-contamination.

The soil was sampled by each replicate in spring for inorganic N and soil analysis. The samples were taken from layers of 0—25 cm and 25—60 cm as explained previously (page 235). Another subsample was taken for inorganic nitrogen determination. These samples were stored frozen (−18 °C) in plastic bags until analysis.

After harvest the plots were sampled to depths of 0—25 cm, 25—60 cm and 60—90 cm. In 1987, two 10 cm subsamples per plot were taken using an engine driven auger. The deeper layers were sampled placing a liner in the hole to avoid contamination of the sample from the layers above it. In 1988, 20 subsamples were taken from the top layer and five subsamples from the deeper layers using a core of 3 cm.

In 1989 and 1990, eight subsamples were taken from each plot using a 5 cm core for the topsoil and a 3 cm core for the subsoil (Fig. 7). These samples were taken using a piece of plywood, where holes were drilled to mark the places of the subsamples. The points were ran-

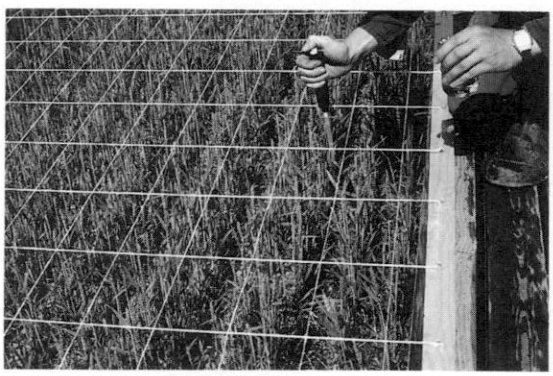


Fig. 6. Pipetting $^{15}N$-labelled fertilizer onto the plots.

Fig. 7. The piece of plywood with the wholes to mark the points of the samples and the sampling equipment.

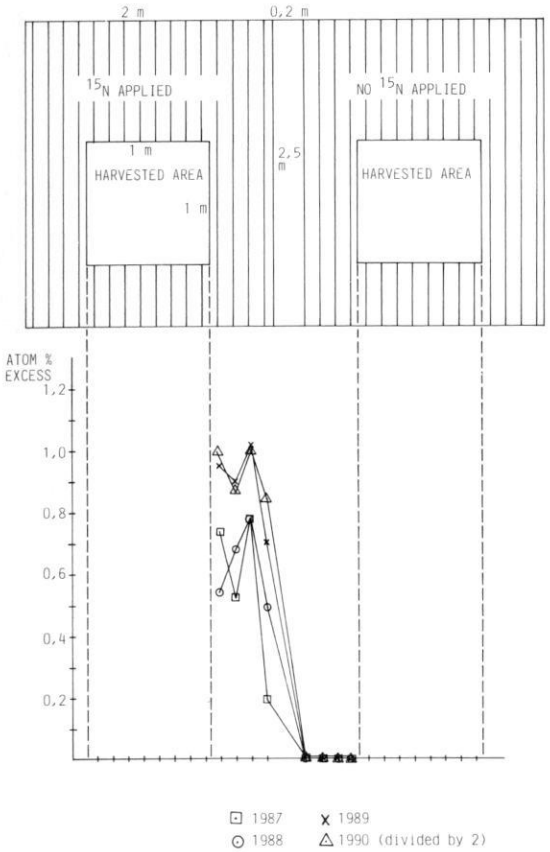



Fig. 8. $^{15}$N excess of the discard rows of the plots where a $^{15}$N fertilized and an unfertilized plot were located side by side. Means of three plots are given.

domized and arranged so that each fertilizer and seed row, and the spaces between the rows were represented in proportion to the area of the plot (RECOUS et al. 1988a). The subsamples were bulked and part of the sample was closed in a plastic bag and deep-frozen for inorganic $^{15}$N analysis, and another part of the sample was dried in 35 °C for total $^{15}$N analysis.

In 1989, the bulked sample from the eight cores was all put up. The sample was sieved (topsoil 6 mm, subsoil 20 mm), the roots were hand picked from the top soil samples and analysed separately, and a subsample was taken like in the other experimental years.

After harvest some discard areas of the plots, where a $^{15}$N fertilized and an unfertilized plot were situated side by side, were sampled row by row at one meter distances. The $^{15}$N content of the rows was analysed individually to control the horizontal movement of the $^{15}$N from one plot to another. The results show that the edge effect was minimal and even a space of 20 cm or one seed row was enough to avoid the cross-contamination between the plots (Fig. 8). This result is in line with the results of VAN-CLEEMPUT et al. (1981) and POWLSON et al. (1986).

## 3.2. Weather conditions

The monthly mean temperatures and precipitation during the growing seasons of the experimental years are presented in Table 5. The 1986 spring was rainy and sowing operations were started late. Sowing was soon followed by a drought period, lasting until mid-July. At

Jokioinen, there was hardly any rain during this period. At Mietoinen, some heavier rain showers occurred around 20 June, which improved the water status of the plants remarkably compared to Jokioinen. After the first rains in July, adventitious tillering started for the plants that had suffered from the drought. The harvesting time and the autumn were rainy.

Also the 1987 spring was late. There was a deep ground frost during the winter and it thawed late, which delayed the drying of the fields and the onset of spring operations. The 1987 summer was cool and rainy. The cool growing season and the frosts, the first frost occurring on 25 August (Jokioinen −3.7 °C), impaired the quality of spring wheat. The experiments could hardly be harvested, and the operation was delayed until October, when the crops were hardly ripe.

The 1988 spring was slightly earlier than normal. The summer was warm and dry until mid-July. The crops suffered from drought, but the onset of rains did not cause adventitious tillering. The experiments were harvested early, at Jokioinen by 10 August and at Mietoinen by 20 August.

The 1989 spring came early, but sowing operations were delayed to normal or later than normal dates by rain. After May with good moisture conditions, the crops suffered from drought especially at Jokioinen until the first heavier rain on 11 July. August was quite rainy, but the experiments were harvested in good condition, and the quality of the yield was good.

The spring operations in 1990 could be started early, at the end of April. The summer was warmer than normal and dry. The drought lasted until the end of June. The sowing of the $^{15}N$ experiment was delayed until normal dates by the lack of $^{15}N$-labelled fertilizer. The experiment was harvested at normal dates, but later than the surrounding crops generally in 1990. The quality of the yield was good.

In conclusion, the period of this research 1986—1990 was characterised by four summers, 1986 and 1988—1990, that were warmer and drier than normal, with an exceptional drought period that lasted from almost the sowing time to about ear emergence. The 1987 summer, on the other hand, was exceptionally cool and wet.

Table 5. Monthly mean temperatures °C (T) and precipitation mm (R) during the growing seasons 1986—90 and the corresponding means for 1931—60 at Jokioinen and Mietoinen (ANON. 1986—1990).

| Month | 1986 | | 1987 | | 1988 | | 1989 | | 1990 | | Mean 1931—60 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | T | R | T | R | T | R | T | R | T | R | T | R |
| | | | | | | Jokioinen | | | | | | |
| May | 10.5 | 52 | 7.6 | 38 | 11.4 | 44 | 10.4 | 41 | 9.3 | 22 | 8.8 | 39 |
| June | 16.3 | 11 | 12.1 | 81 | 16.5 | 25 | 15.4 | 30 | 14.4 | 20 | 13.7 | 42 |
| July | 16.2 | 65 | 14.8 | 68 | 19.0 | 128 | 16.3 | 85 | 15.2 | 85 | 16.2 | 70 |
| August | 12.9 | 110 | 11.7 | 83 | 14.1 | 79 | 13.7 | 92 | 15.0 | 90 | 14.7 | 74 |
| September | 6.4 | 102 | 8.4 | 120 | 10.8 | 85 | 11.0 | 51 | 8.0 | 62 | 9.7 | 61 |
| | | | | | | Mietoinen | | | | | | |
| May | 10.4 | 38 | 7.4 | 45 | 11.0 | 42 | 10.1 | 40 | no experi- | | 8.9 | 25 |
| June | 16.2 | 25 | 11.7 | 91 | 16.3 | 45 | 15.1 | 48 | ments at | | 13.8 | 45 |
| July | 16.4 | 40 | 15.0 | 63 | 19.1 | 104 | 16.4 | 46 | Mietoinen | | 17.1 | 53 |
| August | 13.3 | 149 | 11.9 | 142 | 14.3 | 127 | 14.2 | 106 | in 1990 | | 15.7 | 77 |
| September | 7.4 | 106 | 9.0 | 94 | 11.5 | 71 | 11.8 | 34 | | | 10.6 | 62 |

## 3.3. $^{15}N$ determinations

Six isotopes of nitrogen are known (Table 6). Of the radionuclides of nitrogen, only $^{13}N$ is used in tracer studies, because the other isotopes have too short a half-life for this purpose (HAUCK 1982). The half-life of $^{13}N$, too, is quite short, 603 seconds, which limits its use in labelling.

The stable isotope $^{15}N$ is most commonly used in tracer studies of nitrogen. The $^{15}N$ depleted materials (0.0030—0.0100 atom % $^{15}N$) are used in research less commonly than $^{15}N$ enriched materials. The high cost of $^{15}N$ enriched materials is a limiting factor for their use. $^{15}N$ depleted materials are about 30 % cheaper than $^{15}N$ enriched materials, but they offer a lower accuracy of analytical methods.

There are several methods for the determination of the ratio of the stable isotopes of nitrogen (HAUCK 1982). The two most common methods are mass spectroscopy and optic spectroscopy. The advantage of optic spectroscopy is that it requires a smaller quantity of nitrogen, 0.2—10 µg, compared to mass spectroscopy, 0.5—4 mg. About 10—100 times lower precision is the disadvantage of optic spectroscopy compared to mass spectroscopy. Other methods for $^{15}N$ determination include infrared spectroscopy, electron paramagnetic resonance, nuclear magnetic resonance and microwave spectroscopy, but these are rarely used.

Table 6. The isotopes of nitrogen (ANON. 1981)

| Isotope | Natural abundance | Stability | Half life |
|---|---|---|---|
| $12_N$ | — | radioactive | 0.0125 sec |
| $13_N$ | — | radioactive | 10.08 min |
| $14_N$ | 99.635 atom % | stabile | — |
| $15_N$ | 0.365 » | stabile | — |
| $16_N$ | — | radioactive | 7.35 sec |
| $17_N$ | | radioactive | 4.15 sec |

The nitrogen in the sample has to be released as gaseous $N_2$ before mass spectrometric determination (Fig. 9). The most common method

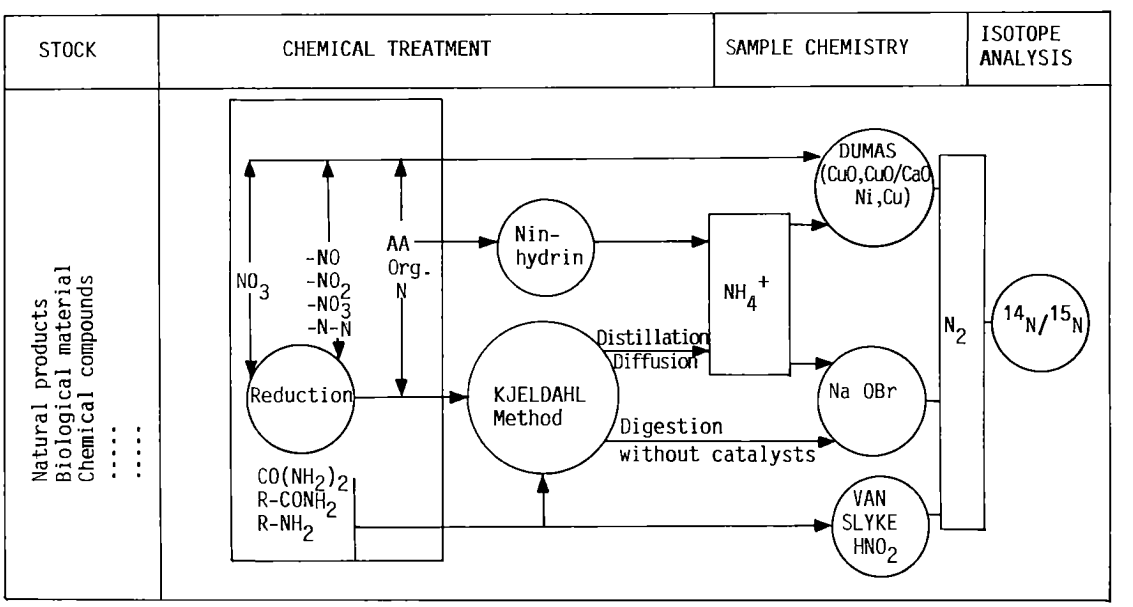



Fig. 9. The pretreatment of samples for $^{15}N$ determination by mass spectrometry (FAUST 1985).

for this is the Kjeldahl method, followed by release of $N_2$ from $NH_4^+$ by hypobromite. Another method for the release of $N_2$ is the Dumas combustion method. An automatic mass spectrometric method based on this has become increasingly popular in recent years (MARSHALL and WHITEWAY 1985, BARRIE and LEMLEY 1989). This method requires less nitrogen in the sample, 10—1000 µg, than the mass spectrometric method based on the Kjeldahl procedure. Other alternatives are the ninhydrin method, diffusion after the Kjeldahl digestion and the Van Slyke method (FAUST 1985).

The method based on the Kjeldahl method and mass spectroscopy was applied in this work for the plant and soil samples in 1987—1988. The salicylic acid-thiosulphate modification of the Kjeldahl method was applied for the analysis of samples from the pot experiment as described by HAUCK (1982). For the field experiments, more sophisticated methods were selected, as described in this section. A method based on automatic Dumas combustion and mass spectroscopy was applied for the samples in 1989 and 1990, and for the protein fractions in the grain and soil inorganic nitrogen analyses of each experimental year.

### 3.3.1. Kjeldahl method for plant and soil material

In principle, the Kjeldahl digestion and distillation before $^{15}N$ determination by mass spectroscopy are done in the same way as the ordinary total nitrogen determination from soil or plant samples. However, some sources of error of minor importance in the ordinary total nitrogen analysis, possibly impairing the result of $^{15}N$ analysis, have to be taken into account (HAUCK 1982).

#### *3.3.1.1. Digestion of the sample*

The nitrogen, mostly amino-N, in a soil or plant sample is digested in the Kjeldahl digestion procedure using sulphuric acid to form $NH_4^+$-N (BREMNER and MULVANEY 1982). Salts, generally $K_2SO_4$ or $Na_2SO_4$, are added to the mixture to raise the boiling point of the digest. Catalysts, e.g. Hg, Cu or Se, are added to increase the oxidation of the organic material in the sample and certain chemicals are added to include the different forms of N, e.g. $NO_3^-$ and $NO_2^-$, in $NH_4^+$-N.

If not all the $NO_2^-$ or $NO_3^-$ or any other poorly reducible nitrogen compounds in the sample, are recovered as $NH_4^+$, the result of $^{15}N$ determination may be altered if the $^{15}N$ enrichment of these compounds is significantly different from the other N containing compounds in the sample. The nitrate or nitrite content of a plant or a soil sample is usually so low that the low recovery does not cause any significant error in the ordinary determination of total nitrogen by the Kjeldahl method. To include the $NO_2^-$ and $NO_3^-$ as $NH_4^+$ in the digest, the salicylic acid-thiosulphate or permanganate-reduced iron modifications of the Kjeldahl method are generally employed. Also Devarda's alloy (LIAO 1981) and a mixture of zinc and chromium(III) (PRUDEN et al. 1985a) have been suggested for this purpose.

In the permanganate-reduced iron modification the sample is first treated with $KMnO_4$ and $H_2SO_4$ to oxidize $NO_2^-$ to $NO_3^-$ and after that with reduced Fe to reduce the $NO_3^-$ to $NH_4^+$ (BREMNER and SHAW 1958). KUMAR and AGGARWAL (1987) showed that zinc can be used instead of iron. As iron used in this method may contain significant amounts of N, its purity should be checked (BREMNER and MULVANEY 1982).

In the salicylic acid-thiosulphate modification the sample is pretreated with salicylic acid dissolved in concentrated sulphuric acid. The reaction between salicylic acid and $NO_3^-$ forms nitro compounds which are reduced to corresponding amino compounds in the acidic solution containing sodium thiosulphate when the mixture is heated.

The ability of the method to recover $NO_2^-$-N quantitatively and the liability of the method for moist soil samples have been questioned (BREMNER 1965), especially if the samples are not finely ground (MORAGHAN et al. 1983). On the other hand, CHENG and BREMNER (1964) and BREMNER and MULVANEY (1982) showed that the method recovers both $NO_3^-$ and $NO_2^-$ nitrogen, as does the permanganate-reduced iron modification. Also PRUDEN et al. (1985b) showed that the salicylic acid-thiosulphate modification gives a quantitative result both in moist and dry soils that are finely ground.

BURESH et al. (1982) and HAUCK (1982) preferred the permanganate-reduced iron modification for soils, because it is more reliable than the salicylic acid-thiosulphate modification, especially if the soils contain significant amounts of nitrite. The permanganate-reduced iron modification is also more reliable if the determination of $^{15}N$ has to be done in a moist soil. BURESH et al. (1982) preferred the salicylic acid-thiosulphate method for plant material, because it is more convenient in routine work applying automatic digestion blocks.

PRUDEN et al. (1985a) suggested that zinc and chromium(III) is used to reduce $NO_3^-$ both in soil and plant samples. The method is based on the fact that chromium(II)sulphate reduces $NO_3^-$ to $NH_4^+$ in a warm dilute solution of sulphuric acid. Because the solutions of chromium(II) are difficult to prepare and store, the chromium(II) is reduced from chromium(III) *in situ* using zinc. This is followed by ordinary Kjeldahl digestion. The method is not suitable for soils containing significant amounts of nitrite.

The ability of salicylic acid-thiosulphate modification (PRUDEN et al. 1985b), permanganate-reduced iron modification (STUMPE et al. 1985) and zinc-chromium modification (PRUDEN et al. 1985a) to recover the added ammonium or nitrate nitrogen from the soils taken from the $^{15}N$ field experiment of the present

Table 7. The recovery of nitrate (4.90 g) or ammonium (4.92 g) nitrogen using the salicylic acid-thiosulphate, permanganate-reduced iron or the zinc-chromium modifications of the Kjeldahl procedure added to topsoil (5.0 g), subsoil (10.0 g) or wheat straw (1.0 g).

| Sample | Topsoil | | Subsoil | | Straw | |
|---|---|---|---|---|---|---|
| | Result N mg | Recovery % | Result N mg | Recovery % | Result N mg | Recovery % |
| Salicylic acid-thiosulphate modification | | | | | | |
| Sample | 10.52 | — | 10.31 | — | 5.41 | — |
| $NO_3^-$-N | 4.85 | 99.0 | 4.87 | 99.4 | 4.92 | 100.4 |
| $NH_4^+$-N | 4.88 | 99.2 | 4.91 | 99.8 | 5.01 | 101.8 |
| Sample + $NO_3^-$-N | 14.60 | 83.3 | 13.72 | 69.6 | 10.26 | 99.0 |
| Sample + $NH_4^+$-N | 15.46 | 100.4 | 15.23 | 100.0 | 10.43 | 102.0 |
| Permanganate-reduced iron modification | | | | | | |
| Sample | 10.54 | — | 10.92 | — | | |
| $NO_3^-$-N | 4.86 | 99.2 | 4.87 | 99.4 | | |
| $NH_4^+$-N | 4.88 | 99.2 | 4.84 | 98.4 | | |
| Sample + $NO_3^-$-N | 15.48 | 100.8 | 15.62 | 95.9 | | |
| Sample + $NH_4^+$-N | 15.56 | 102.0 | 15.77 | 98.6 | | |
| Zinc-chromium modification | | | | | | |
| Sample | 10.38 | — | 10.59 | — | 5.41 | |
| $NO_3^-$-N | 4.21 | 85.9 | 4.15 | 84.7 | 4.18 | 85.3 |
| $NH_4^+$-N | 4.94 | 100.4 | 4.90 | 99.6 | 4.82 | 98.0 |
| Sample + $NO_3^-$-N | 14.84 | 91.0 | 14.71 | 84.1 | 9.59 | 85.3 |
| Sample + $NH_4^+$-N | 15.37 | 10.14 | 15.63 | 102.4 | 10.19 | 97.2 |

study was investigated. The salicylic acid-thiosulphate modification and the zinc chromium modification was also tested using a straw sample. The recovery of $NO_2^-$ was not investigated, because nitrite has only been noticed to accumulate in soils of high pH, where high amounts of fertilizer N had just been added (SCHMIDT 1982), a situation that did not prevail in any of the circumstances of the present study.

The forms of N were added by pipetting 5 ml of solution containing 1 mg/ml N as Ca $(NO_3)_2 \times 4H_2O$ or as $(NH_4)_2SO_4$ to the digestion tube and drying it in an oven at 60 °C. After this the straw or soil was weighed into the tubes. The experiments were made in triplicates.

The salicylic acid-thiosulphate modification recovered the added nitrate nitrogen quantitatively from the nitrate alone or from the plant material, but not from the soils (Table 7). The permanganate-reduced iron modification gave a quantitative result from the pure salt and from the soils. The recovery of nitrate N from the subsoil plus nitrate using 10 g of soil was slightly worse (95.9 %), but better, however, than with the other methods. The result was better when only 5 g of sample was used, probably because of the solid material remaining in the digestion tube, which decreased the recovery if it could not be taken representatively into the subsample taken for distillation of ammonia. The method was not tested in plant material, because it is more laborious than the other two methods tested.

The zinc-chromium modification did not give satisfactory recovery in the nitrate alone, soil, nor in the plant samples. It was decided to use the salicylic acid-thiosulphate modification for plant material and the permanganate-reduced iron modification for soil material.

### *3.3.1.2. Distillation of ammonia and formation of the salt*

After the Kjeldahl digestion the nitrogen is in the form of ammonium N in the digest. The digest is made alkaline with NaOH, and $NH_4^+$-N is steam distilled to an acid (HAUCK 1982). Usually boric acid $H_3BO_3$ is used for collection of ammonia according to the following reaction:

$$NH_3 + H_3BO_3 \longleftrightarrow NH_4^+ + H_2BO_3^-$$

Reducing the so called 'memory effect' is especially important in distillation of digests containing $^{15}N$ (BURESH et al. 1982, PRUDEN et al. 1985b). The surfaces of the apparatus and flasks used in distillation contain small amounts of negative charges, where a small fraction of the ammonia in the samples is adsorbed. This ammonia is exchanged with the ammonia in the subsequent sample. This may give erroneous results of $^{15}N$ determination if the enrichment of the successive samples differs significantly.

The means to reduce the 'memory effect' include generally distillation of ethanol or acetic acid between the samples (HAUCK 1982) or the use of metallic distillation apparatus in stead of glass apparatus, as well as the so called double distillation procedure (PRUDEN et al. 1985b, MULVANEY 1986). Metal surfaces contain less negative charges than glass, which is generally used as a material of distillation apparatus. The double distillation procedure includes distillation of the first aliquot of the digest to determine the N content of the sample. Thereafter a second aliquot is distilled using the same apparatus to collect the ammonia needed for the mass spectrometric determination.

Some laboratories use the Kjeltec-II automatic distillation apparatus for distillation of $^{15}N$ enriched samples. This can be assumed to cause a large 'memory effect', because of the large glass and plastic surfaces in the apparatus.

To reduce the 'memory effect' a metallic dis-

Table 8. The effect of distillation apparatus and ethanol steaming on the $^{15}N$ 'memory effect'. Means of two distillations made by two identical apparatuses are given.

| Enrichment of the sample | Atom % excess $^{15}N$ | | | | |
|---|---|---|---|---|---|
| | Kjeltec-II-apparatus | | Glass apparatus | | Metallic apparatus |
| | No cleaning | Cleaning | No cleaning | Cleaning | No cleaning |
| Unlabelled | 0.0029 | −0.0003 | 0.0003 | 0.0006 | 0.0016 |
| Unlabelled | −0.0007 | 0.0027 | −0.0002 | 0.0003 | 0.0000 |
| Labelled | 4.7254 | 4.8661 | 4.8202 | 4.8220 | 4.8658 |
| Unlabelled | 0.0294 | 0.0181 | 0.0107 | 0.0017 | 0.0060 |
| Unlabelled | 0.0070 | 0.0057 | 0.0035 | −0.0002 | 0.0004 |
| Unlabelled | 0.0033 | 0.0039 | 0.0008 | −0.0001 | 0.0001 |

tillation apparatus was manufactured for this study. The device consisted of the spray trap and condenser inner pipe made of stainless steel, imitating the apparatus of SAFFIGNA and WARING (1977) and PRUDEN et al. (1985b).

The 'memory effect' of the metallic apparatus, a glass apparatus and a Kjeltec-II automatic distillation apparatus was tested with and without distillation of ethanol between each sample (96 %, 30 ml, ca 3 min). The apparatus was first cleaned thoroughly. Then two aliquots of unenriched sample were distilled, followed by a sample of 5 % enrichment, and finally three unenriched samples. Each sample contained 1.5 mg of ammonium nitrogen as $(NH_4)_2SO_4$. The distillate was collected in a slight excess of sulphuric acid. The distillations were made by two identical distillation units as replicates.

The 'memory effect' of the Kjeltec-II apparatus was remarkable even after steaming with ethanol (Table 8). The glass apparatus adsorbed a remarkable amount of $^{15}N$, but the ethanol steaming reduced the amount adsorbed considerably. The metallic apparatus left a clear 'memory effect' in the first sample after the enriched sample. In the second sample the 'memory effect' was so small that it did not cause any significant error in the $^{15}N$ determination. Thus the apparatus is suitable for the double distillation procedure suggested by PRUDEN et al. (1985b). Also the glass distillation unit using ethanol steaming between samples gave equally reliable results, but this procedure is more laborious than the procedure using the metallic apparatus, where no cleaning is required.

To reduce the 'memory effect' it was decided to use the metallic distillation apparatus and a double distillation procedure. The first aliquot was used for determination of N content. The amount of digest needed to give the appropriate amount of N, i.e. 1.2 mg, for isotope ratio measurement was calculated for the second aliquot on the basis of this result.

Also the low recovery of $NH_4^+$-N in the distillate can give erroneous results in the $^{15}N$ determination as a result of incomplete release of $NH_3$ from the digest, loss during the distillation or evaporation from the distillate (HAUCK 1982). Incomplete distillation leads to dilution of the enrichment, because $^{14}NH_3$ is released from the digest slightly more readily than $^{15}NH_3$. The error caused by this is, however, insignificant when working on the accuracy of mass spectrometric determination. The evaporation of $NH_3$ from the distillate can be reduced by efficiently cooling the condenser so that the temperature of the distillate does not exceed 22 °C. In this study the temperature of the distillate was measured from time to time and it ranged between 16 °C and 17 °C.

The ammonium nitrogen content of the boric acid is titrated using for instance sulphuric

acid and a suitable indicator according to the following reaction:

$$H^+ + H_2BO_3^- \longleftrightarrow H_3BO_3$$

In the present study the second aliquot of distillate was evaporated to dryness on a sand bath. The salt was dissolved in about 2 ml of distilled water and the solution was transferred to a 7 ml glass vial and evaporated to dryness in an oven at 80 °C. The vial was capped and stored to await mass spectrometric determination. After use the vial was discarded.

The purpose of this phase is to transfer the $NH_4^+$ nitrogen to ammonium sulphate, because ammonium borate is easily volatilized. In some methods, HCl is used instead of $H_2SO_4$, resulting in the formation of $NH_4Cl$. Ammonium chloride, however, dissociates already in temperatures below 100 °C, making the volatilization of ammonia from the sample and sublimation of $NH_3$ from the surrounding air to the sample possible (HAUCK 1982). This can change the enrichment of the sample, especially when ammonia is present in the air used for evaporation. Sulphuric acid is preferred, because $(NH_4)_2SO_4$ is stable in temperatures up to 235 °C.

The air used for evaporation of the sample should be free from ammonia (HAUCK 1982). This is a measure of precaution that has to be used if, e.g. manure is analysed in the same laboratory. This measure was tested and proved unnecessary. It was not applied in our laboratory, because it hampered the routine work, e.g. by limiting the amount of samples evaporated at the same time.

### *3.3.1.3. The methods applied*

The samples were treated in all phases in order of supposed ascending enrichment of $^{15}N$ to minimize cross-contamination between the samples.

The plant samples were dried at 80 °C. They were ground in a hammer mill (manufactured by Koneteollisuus Oy, Finland) through 1 mm sieve. The mill was cleaned thoroughly between each sample, first with pressure air and then with a cotton-wool plug moistened with ethanol. The ground samples were stored in a plastic bag.

The soil samples were dried at 35 °C. The dried samples were ground in a mortar to pass 1 mm sieve.

**Digestion of plant samples.** The sample was thoroughly mixed and a sample containing about 5 mg of N (1 g straw, 0.25 g grain) was weighed into a 250 ml graduated digestion tube. The samples were analysed in duplicate and each block of 20 tubes contained two reagent blanks. 40 ml of a mixture of salicylic acid and sulphuric acid (50 g salicylic acid in 2 l of $H_2SO_4$ conc.) was added and left overnight at room temperature (for at least 6 h). 5 g of $Na_2S_2O_3 \times 5H_2O$ was then added and the tube was swirled occasionally until frothing ceased. 10 g of $K_2SO_4$, 1g of $CuSO_4 \times 5H_2O$ and 0.1 g of Se were added. The tubes were placed in a 20 place aluminium digestion block (Tecator, Digestion System 20). The temperature was raised first slowly, so that the final temperature of 380 °C was reached in 1 hour. The digestion was continued at this temperature for 3 hours.

After cooling, the digests were made up to volume with distilled water, mixing at the same time vigorously with a test tube mixer. If the digests had solidified on cooling, they were warmed up before adding water.

**Digestion of soil samples.** The sample was mixed thoroughly, and a sample of 5 g of topsoil or 10 g of subsoil was weighed into a graduated 250 ml digestion tube. Each sample was analysed in duplicate and each block of 20 tubes contained two reagent blanks. 10 ml of $KMnO_4$ solution was added (50 g of $KMnO_4$/1 l of water) and the tube was swirled. After 30 seconds, 20 ml of 50 % (v/v) $H_2SO_4$ was added slowly, keeping the tube in an angle of

45° so that the material attached to the walls of the tubes could be rinsed down. After 5 minutes, the tubes were swirled. Two drops of n-octanol were added. 5 g of reduced Fe was then added using a long necked funnel. A glass funnel was placed immediately on top of the tubes and the tubes were swirled. After 15 minutes, the tubes were swirled and placed in a cool digestion block. The digests were heated for 45 minutes at 100 °C and allowed to cool down. 5 g of $K_2SO_4$, 0.5 g of $CuSO_4 \times 5H_2O$, 0.1 g of Se and 20 ml of concentrated $H_2SO_4$ were added and the tubes were placed back in the 100 °C block. The temperature was raised slowly to 240 °C and the samples were digested until the white fumes of $SO_2$ had disappeared. The temperature was raised to 380 °C and the digestion was continued for 5 hours. After cooling the digests were made up to volume with distilled water.

**Distillation of ammonia.** The contents of the tubes were mixed thoroughly. An aliquot of 30 ml of digest was pipetted into a distillation flask. The flask was connected to the spray trap and 20 ml of 10 M NaOH was added down the steam inlet tube. The steam was passed through until 40 ml (10 + 30) of distillate had collected in a decanter dish containing 10 ml of 1 % boric acid — indicator solution. The amount of N was titrated against 0.005 N HCl.

The volume of the second aliquot was such as to contain about 1.2 mg of N. It was pipetted into the distillation flask that was used for the distillation of the first aliquot (after being washed with distilled water). The second aliquot was distilled through the same spray trap as the first aliquot. 40 ml of distillate was collected to a slight excess (ca. 1.05 x) of 0.025 M $H_2SO_4$. This was evaporated to dryness on a sand bath at 80 °C. The dry residue was dissolved in 2 ml of distilled water, transferred into a 7 ml glass vial and evaporated to dryness in an oven at 80 °C. The vial was capped and stored to await isotope ratio measurement. After use the vial was discarded.

*3.3.1.4. Mass spectrometric determination*

The $^{15}N$ enrichment of the samples was determined using a VG Micromass 622 mass spectrometer supplied with an inlet system described by PRUDEN et al. (1985b). The nitrogen was released from the $NH_4^+$ salt as gaseous $N_2$ using alkaline hypobromite according to the following reaction (HAUCK 1982):

$$2NH_3 + 3NaOBr \longrightarrow 3NaBr + 3H_2O + N_2$$

Alkaline sodium hypobromite or lithium hypobromite is generally used for the purpose. Lithium hypobromite is more stable than sodium hypobromite. Lithium hypobromite was used in this work. It was prepared according to the method of ROSS and MARTIN (1970) which is faster and easier than for instance the method for preparation of sodium hypobromite suggested by HAUCK (1982).

There are small amounts of gaseous $N_2$ dissolved in the hypobromite that can cause erroneous results if it is injected into the mass spectrometer together with the sample. To eliminate this bias, helium gas was bubbled through the hypobromite solution for at least one hour before use.

In the reaction releasing the $N_2$, also water and small amounts of $N_2O$ and $NO_3^-$ are released. The mixture of gases contains also other impurities such as ethanol and $CO_2$. Because all these impurities can give erroneous results by increasing either the intensity of the m/e 28 or the m/e 29 peak, they were removed by freezing by liquid nitrogen trap as described by PRUDEN et al. (1985b). When reacting with an acid, the hypobromite also releases some $Br_2$ and $O_2$. This can be avoided by not using too large amounts of acid in the distillation or evaporation of the samples.

An air sample was analysed between each five samples on average. This was done by opening the inlet valve slightly, which gave an air sample of suitable size. The $^{15}N$ content of

this sample was assumed to be of natural abundance, 0.3663 atom %. The daily machine factor (u) was calculated on the basis of the results as follows:

$$u = \frac{y}{x},$$

where

y = natural abundance of $^{15}N$ = 0.3663 atom %

x = measured $^{15}N$ abundance of the air samples

The global variation in the natural $^{15}N$ abundance in the air, 0.3663 (+/−0.0004) %, has been shown to be small by MARIOTTI (1983).

Two reagent blanks were included in each block of 20 samples. The samples were analysed in duplicate. If the difference between the replicates in the N or $^{15}N$ content was greater than 3 %, the determination was repeated.

The $^{15}N$ enrichment in the sample was calculated as follows:

$$x = \frac{100 \times R'}{2 + R'} \times u,$$

where

R' = reading of the $^{15}N/^{14}N$ ratio integrator of the mass spectrometer

u = daily machine factor

The amount of N derived from labelled fertilizer in the sample was calculated as follows (PRUDEN et al. 1985b):

$$F = T\left(\frac{p-q}{f}\right)\left(\frac{t_b}{t_s - t_b} + 1\right)\left(\frac{M_1}{M_2}\right)$$

where

F = weight of N derived from labelled fertilizer in crop or soil sample

T = total weight of N in the sample (µg/g or kg/ha) calculated using an atomic weight of 14 for nitrogen. In calculating T from the titration value $t_s$ the reagent blank $t_b$ is first subtracted. True total N is given by $T\frac{M_3}{M_2}$

p = atom % excess $^{15}N$ in labelled sample of crop or soil (= abundance of $^{15}N$ − natural abundance 0.3663 %)

q = atom % excess $^{15}N$ in control sample of crop or soil that did not receive labelled fertilizer

f = atom % excess $^{15}N$ in labelled fertilizer as added

$t_s$ = volume of $H_2SO_4$ required for titration of distillate from an aliquot of the Kjeldahl digest

$t_b$ = volume of $H_2SO_4$ required for titration of distillate from the same aliquot of the blank Kjeldahl digest

$M_1$ = (true) average atomic weight of N in the labelled fertilizer

$$= \frac{(\text{atom \% } ^{15}N \times 15) + (\text{atom \% } ^{14}N \times 14.003)}{100}$$

$M_2$ = (erroneous) atomic weight (= 14) of N used in calculating the total N content of the sample

$M_3$ = (true) average atomic weight of N in the sample, calculated as for $M_1$

This equation differs from that given by HAUCK and BREMNER (1976) by the two correction factors. The factor $\left(\frac{t_b}{t_s - t_b} + 1\right)$ corrects for N in the Kjeldahl reagents, assuming that the blank titre ($t_b$) is wholly due to reagent N at natural abundance, although the assumption may not be quite true. The factor $\frac{M_1}{M_2}$ corrects for the $M_2$ atomic weight (14) used in calculating the total N content of the crop or soil sample.

The equation of HAUCK and BREMNER (1976) was applied in the study of ESALA (1990) using in part the same research material as the present study. For the present study the results were recalculated using the formula of PRUDEN et al. (1985b). The differences were small if the

blanks were small. If the reagent blanks were higher as they were e.g. in the fractionation of proteins, the differences in the results calculated using these two equations were greater.

### 3.3.2. Automatic $^{15}N$ determination

For the automatic determination the soil and plant samples were finely ground in a disc mill (Siebtechnik, Laboratory Disc Mill, model TS 250) and stored in plastic containers. A sample containing about 100 µg of N (5 mg grain, 15 mg straw, 50 mg soil) was weighed into a small tin cup, which was then sealed and wrapped. Three replicates were weighed from each sample.

The samples were analysed using a Roboprep-CN analyser (supplied by Europa Scientific Ltd, U.K.) linked to the VG Micromass 622 mass spectrometer (Fig. 10) (MARSHALL and WHITEWAY 1985, BARRIE and LEMLEY 1989). This system is known as the ANCA-MS (automated N/C analyzer-mass spectrometer). The VG Micromass 622 is supplied with two collectors (28 and 29) instead of three collectors in the equipment shown in Figure 10.

In this method the sample sealed into the tin capsule drops into a combustion tube (1020°C). This contains $Cr_2O_3$ granules as the oxidation catalyst followed by chopped CuO wire for ox-

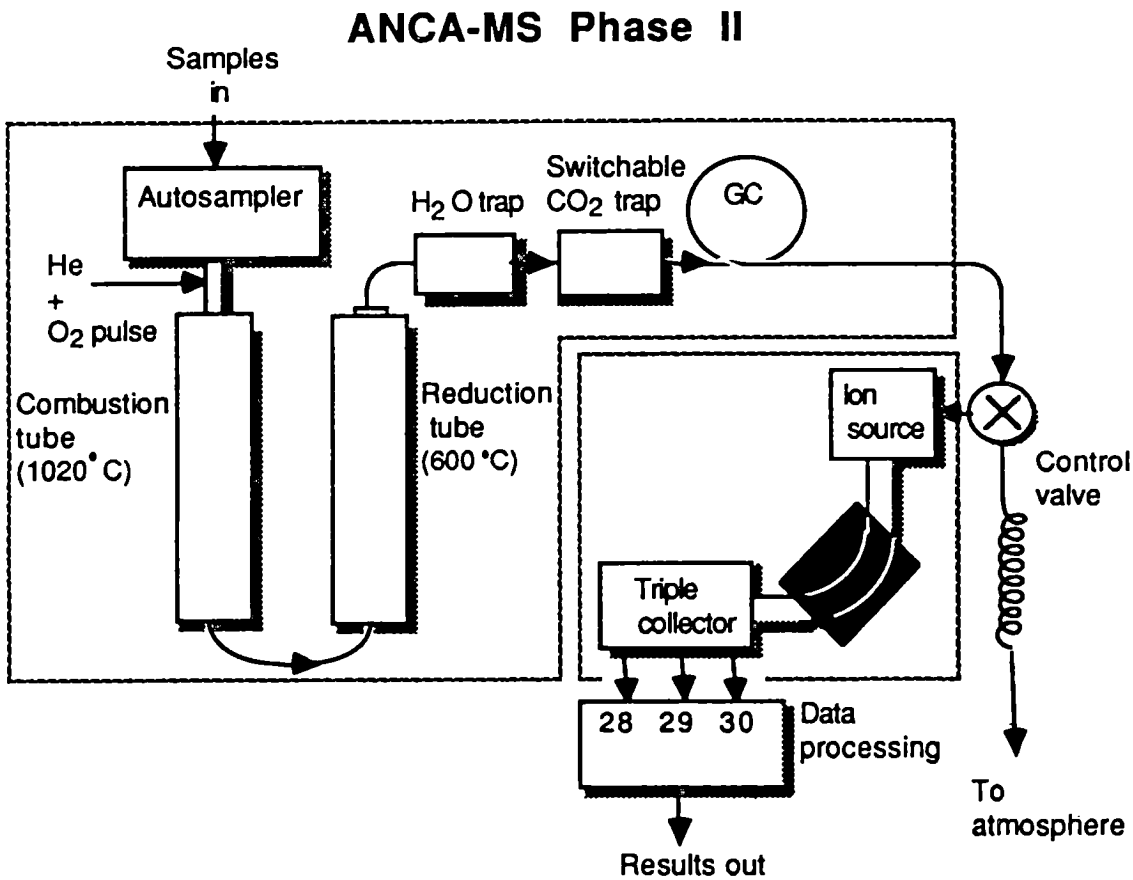



Fig. 10. The automated Dumas combustion method employed by the Roboprep-CN analyser, followed by $^{15}N$ analysis in a mass spectrometer (BARRIE and LEMLEY 1989).

idation of hydrocarbons and Ag wool to trap sulphur and halogens. An oxygen pulse (purity 99.998 %) is injected into the tube and flash combustion of the tin cup raises the local temperature to 1700 °C. Combustion products ($CO_2$, $N_2$, $NO_x$ and $H_2O$) are swept by a He carrier gas (purity 99.998 %) into a reduction tube (Cu wires, 600 °C), where oxides of nitrogen are reduced to $N_2$. Water is removed in a water trap containing magnesium perchlorate and $Co_2$ in a trap containing Carbosorb (Elemental Microanalysis Ltd, U.K.). A small portion (about 1 %) of the gas is fed to the mass spectrometer through a capillary interface. The gas is analysed for total nitrogen and $^{15}N$ in the mass spectrometer. Each cycle of one sample takes about 5 minutes and the run is controlled by a microcomputer.

The samples were run against a reference sample containing 0.5 % N and assumed to contain the natural enrichment, 0.3663 %, of $^{15}N$. It was prepared by pipetting 20 µl of solution containing the desired amount of N as $(NH_4)_2SO_4$ into tin cups containing Chromosorb P (Elemental Microanalysis Ltd, U.K.) and drying it in an oven at 80 °C. The reference sample was run between every set or every second set of triplicated samples.

The results were calculated in the same way as the results based on the Kjeldahl pretreatment of the samples except for the machine factor and the correction factor for the reagent blanks, for they are included in the automated analysis of the samples.

The automated method was comparable to the previous method based on the Kjeldahl digestion in the tests made before the new system was introduced. Also a standard sample of wheat straw containing 1.07 % N and 1.3844 atom % $^{15}N$ expressed as means of 20 replicates of determinations using the Kjeldahl method was analysed in duplicate at the end of each batch of samples to control the reliability of the run. The means of 30 randomly selected runs of these standards were 1.10 % N and 1.3798 atom % $^{15}N$. So the results of nitrogen determination with the automatic method was 102.8 % and that of the $^{15}N$ determination 99.7 % of the results by the method based on the Kjeldahl digestion. The higher result of nitrogen determination based on the Dumas combustion compared to the Kjeldahl method is in agreement with previous investigations (e.g. JENSEN 1991).

### 3.3.3. Fractions of proteins in the grain

The seed proteins were fractionated into four fractions according to their solubility in 1) 1 M NaCl, 2) 70 % ethanol, 3) 50 % 1-propanol + 2 % 2-mercaptoethanol + 1 % acetic acid and 4) insoluble residue fraction (SAARINEN 1990, unpublished method). The non-protein nitrogen was separated from fraction 1 using 10 % TCA and 0.1 M NaOH solution. The amount of flour weighed for the fractionations was 0.6 mg DM. Fraction 1 consists mainly of albumins, globulins and nonprotein nitrogenous compounds, fraction 2 of gliadins, fraction 3 of glutenins and fraction 4 of structural proteins and starch (MIFLIN et al. 1983, SHEWRY et al. 1986).

The fractions were digested using the Kjeldahl method. A metal distillation apparatus and ethanol cleaning procedure were employed in distillation of the samples instead of the double distillation procedure used for the ordinary $^{15}N$ analysis. After evaporation of the distillates the salt was dissolved in water and 20 µl of this solution was injected into tin cups containing Chromosorb P and analysed for $^{15}N$ using the automatic system. The amount of water for dissolving the salt was usually 0.15—0.30 ml and it was calculated so that 100 µg nitrogen was brought into the tin cups.

Each fraction of a certain sample was analysed in duplicate and each duplicate was further analysed for $^{15}N$ in duplicate. So, a certain fraction of each yield from a certain pot was analysed for $^{15}N$ in four replicates. The non-

protein nitrogen was determined without replicates, but each solution was analysed for $^{15}N$ in triplicate.

The grain from the pot experiment was ground for the fractionations in the hammer mill through a 0.8 mm sieve. The grain from the field experiments was ground in the disc mill which yielded much finer flour than the hammer mill.

### 3.3.4. Extractable inorganic nitrogen in soil

The exchangeable inorganic forms of nitrogen in soil are mainly $NH_4^+$ and $NO_3^-$, in some cases also $NO_2^-$ ions, which are usually extracted with salt solutions such as 2 M KCl (KEENEY and NELSON 1982). Although there are other inorganic forms of nitrogen in soil, the most important of them being the nonexchangeable $NH_4^+$ fixed in the interlayer positions of some clay minerals, this extractable inorganic nitrogen is often termed inorganic nitrogen in soil, as also later in the present study.

For the inorganic nitrogen and $^{15}N$ analysis the frozen soil samples were thawed overnight at 5 °C. The soil was homogenized and 100 g of moist soil was weighed and 250 ml of 2 M KCl added followed by shaking for 2 hours. The suspensions were filtered and the extracts were stored at 5 °C. The samples were analysed in duplicate. The dry matter content of the soil was also determined (40 g moist soil, 105 °C overnight). All the samples for inorganic nitrogen were analysed in spring 1991. So the samples were stored frozen 0.5—3.5 years.

The ammonium and nitrate N contents of the extracts were analysed by a Skalar autoanalyser. Ammonium nitrogen is analysed in the analyser by a modified Berthelot reaction by forming an indophenol blue complex (VERDOUW et al. 1977, KROM 1980). Nitrate nitrogen is analysed by forming a diazo complex after reduction to nitrite in a cadmium column (HENRIKSEN and SELMER-OLSEN 1970, GREENBERG et al. 1980).

The $NH_4^+$-N and $NO_3^-$-N content of the soil, expressed in mg/kg DM, was calculated from the results of colorimetric determination and dry matter determination of the soil. The soil moisture was taken into account when calculating the ratio of extractant/soil by adding the amount of water in the fresh soil to the amount of the KCl and subtracting the respective amounts from 100 g of fresh soil.

The amounts of $NH_4^+$-N and $NO_3^-$-N in the soil, expressed in kg/ha, were calculated on the basis of these results and the volume-weight determination of the soil. This was determined by taking a sample of soil using a 5 cm core of a certain volume from the field and drying it in 105 °C until no drop in the weight was noticed (usually overnight). The whole equation for the calculation of the results was as follows:

$$x = (c - b) \times U \times h \times m$$

where

x = amount of $NH_4^+$-N or $NO_3^-$-N in kg/ha
c = corresponding concentration in the extract in mg/l
b = value of reagent blank in mg/l
U = ratio of extractant/soil corrected with soil moisture content in ml KCl/g soil
h = depth of sampling in dm
m = volume weight of soil in kg DM/dm$^3$

The inorganic $^{15}N$ in the soil extracts was analysed by a microdiffusion method modified by BROOKS et al. (1989). A 50—100 ml volume containing about 50—100 µg of N of the soil extract was weighed into a 250 ml plastic bottle (Fig. 11). Devarda's alloy (0.4 g) and MgO (0.2 g) were added to the extract. An acid washed glass bead was added to improve the mixing of the solution. Immediately after that a 7 mm diameter glass fiber disk (Whatman GF/D) containing 10 µl of 2.5 M $KHSO_4$ and held by a stainless steel wire was put in the bottle and the bottle was capped. Before that the disc with the acid was dried in a desiccator over

$H_2SO_4$ conc. This amount of $KHSO_4$ can absorb 350 µg of nitrogen. The container was mixed carefully against the top of the table for 15 seconds, not allowing the solution to come into contact with the glass fiber disk. Each extract was analysed in duplicate if enough N was obtained in 50 ml of extract.

After diffusion for seven days at room temperature the glass fiber disk was removed and dried over $H_2SO_4$ conc. in a desiccator and wrapped in a tin cup await for the automatic mass spectrometric determination. At the same time a reagent blank and a standard solution containing 100 µg N 1.3642 atom % $^{15}N$ as ammonium sulphate was diffused.

The diffusion method included more problems than reported by BROOKS et al. (1989). The problems were mostly caused by the reagent blank, usually 10—12 µg N. Much effort had to be put on the method to get constant reagent blanks, but after reaching this the method was shown to be as reliable as steam distillation of inorganic nitrogen.

To test the source of the nitrogen in the blanks, 100 µg of $NH_4^+$-N was diffused or steam distilled (KEENEY and NELSON 1982) from 50 ml of KCl or water solutions using either MgO (0.4 g) or NaOH (0.5 ml, water solution 1/1 v/v) to release the $NH_3$ from the solution.

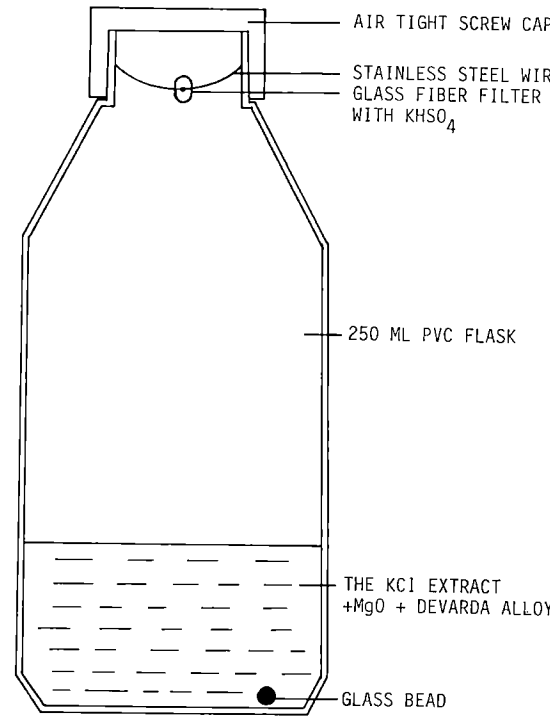



Fig. 11. Diffusion and trapping of $NH_3$ released from the soil extracts.

MgO was used with or without reduction of nitrate with Devarda's alloy. A reagent blank using only water or KCl was diffused at the

Table 9. The effect of different reagents to release nitrogen from 50 ml KCl solution or water on microdiffusion of 100 µg of ammonium nitrogen and on the reagent blanks.

| Sample | Diffused | | | Distilled |
|---|---|---|---|---|
| | Recovery of N in discs | Atom % enrichment | Corrected by blank | Atom % enrichment |
| KCl + MgO | 89.5% | 1.3149 | 1.3377 | 1.2981 |
| KCl + MgO + Devarda | 90.8% | 1.2194 | 1.3481 | 1.2408 |
| KCL + NaOH | 89.7% | 1.3169 | 1.3475 | 1.2969 |
| $H_2O$ + MgO | 68.1% | 1.3514 | 1.3514 | 1.3311 |
| $H_2O$ + evaporated to dryness (not diffused) | | 1.3264 | | |
| blanks: KCl + MgO | | 2.1 µg | | |
| KCl + MgO + Devarda | | 11.9 µg | | |
| KCL + NaOH | | 2.8 µg | | |
| $H_2O$ + MgO | | 0.0 µg | | |

same time. All the determinations were made in four replicates.

Most of the blank was noticed to be caused by nitrate, either from the reagents, KCl or water (Table 9). The blanks were corrected using the equation (SØRENSEN and JENSEN 1991): Atom % $^{15}N$ corrected

$$= \frac{\mu g\ N \times \text{atom}\ \%\ ^{15}N\ \text{measured} - \mu g\ N\ \text{blank} \times 0.3663}{\mu g\ N\ \text{measured} - \mu g\ N\ \text{blank}}$$

After blank correction the method gave satisfactory results. The calculated atom % for the ammonium sulphate standard was 1.3642. So the diffused values were 98.1—99.1 % of the calculated values. The enrichment of the ammonium sulphate standard was 1.3678 atom % determined after evaporation of a small subsample. The low results after distillation of the samples show that they are also diluted by a blank.

The effect of the amount of ammonium or nitrate nitrogen, or a mixture of both, or the amount of solution on the accuracy of the diffusion method was tested. Either 50 or 100 µg of both forms of nitrogen, separate or mixed, was diffused from 50 ml KCl solution. The 100 µg amount of N was also diffused from 100 ml of KCl. After diffusion the glass fiber discs were analysed for total N and $^{15}N$. The diffused solutions were filtered and analysed for ammonium and nitrate nitrogen by an autoanalyser. The enrichment of ammonium, as determined from an evaporated sample of the stock solution, was 1.3678 atom % and that of nitrate 2.4553 atom %. So, the calculated enrichment of the mixture was 1.9116 atom %.

The release of nitrogen from the solutions was almost complete (Table 10). Less than 2 % of the nitrogen originally present in the diffused solution was retained there after diffusing 50 ml of solution. The corresponding figure for 100 ml of solution was below 4 %. The recovery of N in the discs was only 70—90 % of the amount of nitrogen in the solution. About 10—30 % of the nitrogen in the solutions was not recovered from the system as ammonia. The reason cannot be leaking during the diffusion, because the bottles were air-proof. The most probable reasons were that all the ammonia was not absorbed by the disc or a part of it was retained in the solution in other compounds. The low recovery, however, did not have any effect on the reliability of the results as shown previously by BROOKS et al. (1989), BURKE et al. (1990) and JENSEN (1991). The blanks were the same for 50 ml and 100 ml of KCl, i.e. 10.8 and

Table 10. The results of microdiffusion or distillation of 50 or 100 µg of ammonium or nitrate nitrogen from 50 ml of 2 M KCl or 100 µg of ammonium or nitrate nitrogen from 100 ml of the corresponding solution or evaporating the corresponding treatments of water solution.

| Form of N | N µg | Solution ml | Retained in solution % | Recovered in discs | | Atom % $^{15}N$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Uncorrected | | | Corrected |
| | | | | µg | % | Diffused % | Distilled | Evaporated | Diffused |
| $NH_4^+$ | 50 | 50 | 0.9 | 51.7 | 86.7 | 1.1444 | 1.0813 | 1.2831 | 1.3499 |
| $NH_4^+ + NO_3^-$ | 50 | 50 | 0.0 | 53.1 | 90.4 | 1.5738 | 1.5141 | 1.8340 | 1.8821 |
| $NO_3^-$ | 50 | 50 | 0.0 | 52.0 | 89.0 | 1.9995 | 1.8485 | 2.4490 | 2.4276 |
| $NH_4^+$ | 100 | 50 | 1.8 | 93.3 | 86.0 | 1.2276 | 1.2044 | 1.2976 | 1.3403 |
| $NH_4^+ + NO_3^-$ | 100 | 50 | 1.6 | 91.8 | 82.9 | 1.7147 | 1.6837 | 1.8807 | 1.8945 |
| $NO_3^-$ | 100 | 50 | 0.9 | 92.7 | 82.3 | 2.1898 | 2.0957 | 2.4544 | 2.4303 |
| $NH_4^+$ | 100 | 100 | 3.7 | 76.8 | 71.4 | 1.2124 | 1.2096 | 1.2825 | 1.3304 |
| $NH_4^+ + NO_3^-$ | 100 | 100 | 3.5 | 72.1 | 67.1 | 1.6625 | 1.6532 | 1.9363 | 1.8568 |
| $NO_3^-$ | 100 | 100 | 2.3 | 75.4 | 71.3 | 2.1518 | 2.0713 | 2.4372 | 2.4061 |

9.4 µg respectively, as also noticed by SØRENSEN and JENSEN (1991).

After diffusion the blank corrected enrichments of $^{15}N$ in the solutions containing 50 or 100 µg N in 50 ml of 2 M KCl or 100 µg N in 100 ml KCl were all within the range 97.1—99.0 % of that of the stock solution. The enrichments of the corresponding steam distilled solutions showed again the presence of some nitrogen in the reagents introducing a blank. A blank correction factor should also be applied to the results of steam distillation, if this blank can be determined accurately.

The slightly lower values for the diffused samples compared to the calculated value may be due to slightly too low blank values. The blank values of 10—12 µg are at the lower limit of accuracy of the Roboprep-CN-mass spectrometer system, which may cause some bias in the results. The water used for the solutions may also contain some nitrogen, which causes dilution of the enrichments. This can also explain the lower enrichments of the evaporated samples.

In the preliminary tests six days was a long enough time to obtain maximum release of both $NO_3^-$ and $NH_4^+$-N from the solution and maximum recovery in the discs as shown by BROOKS et al. (1989).

The GF/D type glass fiber discs absorbed better the water concentrated on the disc than the GF/C discs. This gave better recoveries of N and better results, probably because water dropping from the discs back to the solution was avoided.

The diffusion method was applied in the present study, because it is less tedious and time-consuming than the steam distillation method of KEENEY and NELSON (1982). The problem of blanks is also obvious when using the steam distillation method for small amounts of nitrogen in the extracts. Usually, in this method, the small amounts of nitrogen are spiked with extra nitrogen, which also causes problems in the accuracy of the method. This measure is not necessary in the diffusion method. However, the diffusion method has to be tested carefully before use.

### 3.4. Other analyses

The particle size composition of the inorganic matter in soil samples was determined by the pipette method of ELONEN (1971), organic C content by the dry combustion method of SIPPOLA (1982) and total N by the Kjeldahl digestion followed by colorimetric determination of ammonia using an AKEA autoanalyser (ANON. 1986). Soil $pH_{water}$ was determined potentiometrically (soil/water = 1/2 v/v) using glass electrodes. Extractable macronutrients in the soil were determined by extracting with acid ammonium acetate (VUORINEN and MÄKITIE 1955). The extractable ammonium and nitrate nitrogen content of the soil in spring was analysed from frozen soil samples by extracting in 2 M KCl overnight and analysing the extracts by a Skalar autoanalyser in the same way as the samples for inorganic $^{15}N$ content.

The total nitrogen content of the grain was determined by the NIR technique (MCGUIRE 1986) and the crude protein content was calculated by multiplying the result with the factor 5.7. The baking quality of the yield was tested by the method of the Research Laboratory of the Finnish Grain Board (HUTTUNEN et al. 1980, HÖMMÖ et al. 1991). Baking quality was tested only if the Hagberg falling number of the flour exceeded 120. Dough properties were determined by Brabender's farinograph and extensograph according to the ICC stan-

dards 115 and 114, respectively (ICC 1972a and b). The Hagberg falling number was determined by a falling number apparatus (ICC standard 107, ICC 1968), and the wet gluten content by the Glutomatic gluten washing apparatus (ICC standard 137, ICC 1982).

The test weight of the grain was determined by weighing four volumes of 250 ml with a special apparatus according to the official method of the State Seed Testing Station of Finland (ANON. 1979). The 1000 grain weight was determined by weighing four samples of 100 grains. The baking test, Hagberg falling number, wet gluten content, test weight and 1000 grain weight were determined from the pooled samples of the replicates.

### 3.5. Statistical methods

The statistical analyses of the results were calculated using a VAX 11/780 computer and the GLM (General Linear Model) procedure of the SAS statistical program (ANON. 1985). The effects of the experimental treatments on the measured properties were tested with the analysis of variance. Statistical significance of differences was considered at the 95 % probability level with Tukey's studentized range test (HSD, Honestly Significant Difference) (STEEL and TORRIE 1980). The differences between control treatments and other treatments were tested using the contrast statement of the GLM procedure (ANON. 1985).

Statistical significance of differences is expressed with asterisks, one asterisk (*) indicating a difference at the 95 % ($P = 0.05$), two asterisks (**) at the 99 % ($P = 0.01$) and three asterisks (***) at the 99.9 % confidence level ($P = 0.001$) and ns indicates no statistical significance ($P > 0.05$).

## 4. THE EFFECT OF TIME OF APPLICATION AND FORM OF NITROGEN FERTILIZER APPLIED AS TOP DRESSING

### 4.1. Introduction

The principle of top dressing part of the fertilizer dose is based on the observations that splitting the fertilizer application may increase the yield potential and the protein content by providing the crops enough nitrogen at grain filling (NATR 1972, LANGER and LIEW 1973, SPIERTZ and ELLEN 1978, DARWINKEL 1983). DARWINKEL (1983) showed that maximum tiller formation and spikelet initiation was stimulated when extra nitrogen was applied at the beginning of tillering, maximum ear number was stimulated by nitrogen applied at the onset of stem elongation, maximum grain number per ear by nitrogen applied during stem elongation until flag leaf emergence and single grain weight by nitrogen applied at ear emergence.

Three commercial fertilizers suitable for top dressing of crops, calcium ammonium nitrate, calcium nitrate and urea, are on the market in Finland. In calcium nitrate, 91 % of the nitrogen is in nitrate form and 9 % in ammonium form (ANON. 1989). Half of the nitrogen in calcium ammonium nitrate is in nitrate and the other half in ammonium form.

It can be assumed that because the nitrate nitrogen is only weakly bound to the soil colloids it is easily movable to the plant roots. On the other hand, it is more easily removed from the soil by leaching or by denitrification than ammonium nitrogen which is adsorbed by the soil particles more intensively and is thus less movable than nitrate ion. However, ammonium is nitrified even in a few days (NISHIO and FUJIMOTO 1990) or in a few weeks (RECOUS et al. 1988a, WILD 1988) in ample moisture and temperature.

Urea is decomposed rather rapidly in soil in favourable conditions by enzymatic activity to carbon dioxide and ammonium nitrogen (LADD and JACKSON 1982, RECOUS et al. 1988a). In a soil of high pH the ammonium nitrogen released from urea can be volatilized (BACON et al. 1986), especially because the pH of the soil is raised by the reaction of decomposition for a short time in the immediate vicinity of the urea granule (SINGH and BEAUCHAMP 1989). Because the Finnish soils are relatively acid, the volatilization losses from urea fertilizers are rather small. They have been estimated to be less than 20 % in Finland (NISKANEN et al. 1990).

Urea can also be foliarly applied to crops. Most of the applied urea is translocated in a few hours mostly through the cuticle to the leaves (HUNDT et al. 1990). There it is metabolized by the urease enzyme rather rapidly, in two to four days, to ammonium nitrogen. This, in turn, is used in the amino acid synthesis of the plant (HARPER 1984, KARASUYAMA et al. 1985, TURLEY and CHING 1986, CHEN and CHING 1988).

## 4.2. Results from the field experiment

The experimental design can be used to answer the following questions: Do the top dressing treatments differ in their effect on the characteristics investigated? Do the control treatments differ from the top dressing treatments in their effect on these characteristics? Do the fertilizer practices have any effect on these characteristics.

### 4.2.1. Yield, protein content and nitrogen yield

*Top dressing treatments*

In top dressing treatments the form of fertilizer applied had no statistically significant effect on the yield of spring wheat calculated as means of the experimental locations, years and varieties (Table 11). The effect on the protein content was statistically significant. Foliar application of urea resulted in statistically significantly lower protein content in the grain than calcium ammonium nitrate (***) calcium nitrate (***) or granular urea (**). The time of top dressing did not affect the yield statistically significantly, but the later application resulted in a statistically significantly higher protein content of 0.2 percentage units than the earlier application.

The yield was affected statistically significantly by the fertilizer in five out of 16 single cases of experiments and varieties and by the time of application in one case (Appendices 1—2). The yield of Heta was affected by the fertilizer in the experiments at Mietoinen in 1988 and 1989 and the yield of Kadett in the experiments at Jokioinen in 1986 and 1989 and at Mietoinen in 1989. The later application yielded better in Heta at Mietoinen in 1987. The results of the effect of a certain fertilizer applied by top dressing on yield were contradictory and no clear trends could be observed.

The protein content was affected more frequently than the yield; by the fertilizer in five

of 14 cases and by the time of application in three of 14 cases (Appendices 3—4). The interaction of fertilizer and time of application was statistically significant in four of 14 cases. Granular fertilizers, especially CAN and CN, were superior to foliar application of urea in the experiments with statistically significant effect of fertilizer on the protein content. In all the three cases with statistically significant effect of the time of application on protein content the later application increased the protein content. For the experiments at Mietoinen in 1986 no statistical analysis could be made because the protein content was not analysed separately from each replicated plot; but the samples from the replicates were pooled.

*Control treatments vs. top dressings*

When 140 kg/ha of nitrogen was given as one dressing at sowing, the highest yield and almost an equally high protein content were obtained compared with splitting the fertilizer dose to a 100 kg/ha spring application and 40 kg/ha top dressing during the growing season. The growth regulator application reduced the yield depression caused by lodging, but decreased the protein content by 0.3 percentage units corresponding to the yield increase. The yield of

Table 11. The effect of top dressing of various forms of nitrogen on the yield, nitrogen yield and protein content of spring wheat in 1986—1989. Means of two varieties and two experimental sites are given.

| Fertilizer application | Yield kg/ha | Protein content % | Nitrogen yield kg/ha |
|---|---|---|---|
| 100 kg/ha N in spring | 3230 | 13.7 | 64.4 |
| 140 kg/ha N in spring | 3480 | 14.5 | 73.4 |
| 140 kg/ha N in spring + CCC | 3590 | 14.2 | 74.6 |
| 100 » + 40 kg/ha N as CAN, tillering | 3340 | 14.6 | 71.6 |
| 100 » » ear emergence | 3320 | 14.8 | 72.0 |
| 100 » + 40 kg/ha N as CN, tillering | 3370 | 14.8 | 72.8 |
| 100 » » ear emergence | 3320 | 15.1 | 73.7 |
| 100 » + 40 kg/ha N as urea, granular, tillering | 3340 | 14.5 | 71.1 |
| 100 » » » » ear emergence | 3310 | 14.8 | 71.7 |
| 100 » + 40 kg/ha N as urea, foliar, tillering | 3340 | 14.4 | 70.4 |
| 100 » » » » ear emergence | 3350 | 14.3 | 70.0 |
| Fertilizers for top dressing | | | |
| CAN | 3330 | 14.7 | 71.8 |
| CN | 3350 | 14.9 | 73.3 |
| Urea, granular | 3320 | 14.7 | 71.4 |
| Urea, foliar | 3350 | 14.4 | 70.2 |
| Times of application of top dressing | | | |
| Tillering | 3350 | 14.6 | 71.5 |
| Ear emergence | 3320 | 14.8 | 71.9 |
| Statistical significance of differences | | | |
| All treatments except unfertilized | | | |
| Fertilizer | *** | *** | *** |
| 140 kg/ha N in spring vs. top dressings | | | |
| Fertilizer | ns | *** | ns |
| Time of application | ns | * | ns |
| Fertilizer * time of application | ns | ns | ns |
| Top dressings only | | | |
| Fertilizer | ns | *** | ns |
| Time of application | ns | * | ns |
| Fertilizer * time of application | ns | ns | ns |

the crops was reduced by 3—5 %, when comparing the top dressings with the corresponding amount of spring applied nitrogen. In the protein content the results of the top dressed plots varied from a reduction of 0.2 percentage units to an increase of 0.6 percentage units.

Compared to spring application of 100 kg/ha nitrogen the extra 40 kg/ha increased the protein content of the grain by 0.8 percentage units when applied in spring and by 0.6 to 1.4 percentage units applied as top dressing. The yield increased by 8 % by the spring application and by 2—4 % by top dressing.

All the yields obtained by the top dressings of nitrogen were statistically significantly lower than the yields obtained by both spring applications of 140 kg/ha of nitrogen. The yields obtained by the spring application of 100 kg/ha of nitrogen did not differ statistically significantly from the top dressings.

The protein contents in the grain of the control treatments of 100 kg/ha and 140 kg/ha of nitrogen + growth regulator were statistically significantly lower than those of the top dressings (***). According to the general linear models procedure, these control treatments differed statistically significantly from all the single top dressing treatments except the difference between the 140 kg/ha nitrogen + growth regulator and foliar-applied urea.

From single experiments comparing the spring applied 140 kg/ha nitrogen with the top dressings the yield was affected by the fertilizer in six of 16 cases and by the time of application in one case (Appendices 1—2). Except for Luja at Mietoinen in 1986 the cases were the same as when comparing top dressings alone. The protein content was affected by the fertilizer in five of 14 cases and by the time of application in three of 14 cases. The interaction of fertilizer and time of application on the protein content was statistically significant in four of 14 cases. Again, the cases were the same as when comparing the top dressing treatments alone.

The results for the yield were contradictory, but the yield was in most cases higher with spring applied 140 kg/ha nitrogen. The protein content was higher more frequently with top dressing than when applying the total amount of nitrogen in spring. The yield and protein content never increased simultaneously by top dressing compared to application of the total amount of nitrogen in spring.

The nitrogen yield increased by 5.6—10.2 kg/ha by the extra 40 kg/ha compared to the basic application of 100 kg/ha nitrogen (Table 11). This increase was statistically significant (***). The spring application of 140 kg/ha nitrogen did not differ statistically significantly from the top dressings. The nitrogen yield of the control treatment of 140 kg/ha nitrogen and growth regulator was the highest and statistically significantly higher than the nitrogen yields of both the urea applications (* and **, respectively). The top dressing treatments did not differ from each other statistically significantly.

### 4.2.2. Lodging, falling number, test weight, thousand grain weight and wet gluten

Top dressing part of the fertilizer did not reduce lodging of the crops statistically significantly compared to applying the corresponding amount of 140 kg/ha nitrogen as one dressing combine drilled in spring or split as top dressing (Table 12). However, the effect of time of application of the extra 40 kg/ha nitrogen was statistically significant. The later the dressing was applied, the less lodging occurred. Also on the plots applied 140 kg/ha nitrogen + growth regulator lodging occurred statistically very significantly less than on the top dressed plots. In many of the experiments there was no lodging at all, which decreased the differences in the mean values. The trends and the statistical signifigances in the means calculated from the years when considerable lodging was observed were, however, the same as those cal-

culated from all the results (results not shown).

The experimental treatments did not affect the Hagberg falling number, test weight or thousand grain weight statistically significantly (Table 12).

The wet gluten content of the flour was only determined from the yields of 1986, 1988 and 1989. In 1987, the gluten content was so low that it could not be determined accurately. The application of 100 kg/ha nitrogen in spring resulted in statistically significantly lower gluten content compared to the top dressing treatments (Table 12). Also the application of 140 kg/ha of nitrogen with growth regulator yielded lower gluten contents than the top dressing treatments, except for urea spraying.

The time of application of the extra 40 kg/ha of nitrogen also affected statistically significantly the wet gluten content of the flour. The later the fertilizer was applied the higher was the wet gluten content, although the difference between spring application and application at ear emergence was only 1.8 percentage units.

### 4.2.3. Baking quality

Complete baking tests could only be made from the yields of 1988 and 1989. In the other experimental years the falling number was too

Table 12. The effect of top dressing of nitrogen on the lodging, falling number, test weight, thousand grain weight and wet gluten of spring wheat. The results are means of both of the experimental sites and varieties in 1986—89. Wet gluten content is given as means of the years 1986, 1988 and 1989.

| Fertilizer application | Lodging % | Falling number | Test weight kg/hl | Grain weight g/1000 | Wet gluten % |
|---|---|---|---|---|---|
| 100 kg/ha N in spring | 17 | 216 | 75.4 | 33.7 | 36.4 |
| 140 kg/ha N in spring | 24 | 201 | 74.8 | 33.6 | 41.9 |
| 140 kg/ha N in spring + CCC | 10 | 217 | 75.0 | 33.1 | 40.8 |
| 100 » + 40 kg/ha N as CAN, tillering | 22 | 198 | 75.0 | 33.6 | 42.1 |
| 100 » » ear emergence | 20 | 201 | 75.4 | 34.2 | 44.5 |
| 100 » + 40 kg/ha N as CN, tillering | 23 | 196 | 75.0 | 34.1 | 44.2 |
| 100 » » ear emergence | 22 | 194 | 75.2 | 34.1 | 46.4 |
| 100 » + 40 kg/ha N as urea, granular, tillering | 22 | 204 | 75.1 | 33.7 | 42.9 |
| 100 » » » » ear emergence | 18 | 203 | 75.5 | 34.2 | 42.8 |
| 100 » + 40 kg/ha N as urea, foliar, tillering | 21 | 202 | 75.1 | 33.9 | 40.8 |
| 100 » » » » ear emergence | 19 | 200 | 75.4 | 33.8 | 41.3 |
| Fertilizers for top dressing | | | | | |
| CAN | 21 | 200 | 75.2 | 33.9 | 43.3 |
| CN | 23 | 195 | 75.1 | 34.1 | 45.3 |
| Urea, granular | 20 | 204 | 75.3 | 34.0 | 42.8 |
| Urea, foliar | 20 | 201 | 75.3 | 33.9 | 41.0 |
| Times of application of top dressing | | | | | |
| Tillering | 22 | 200 | 75.1 | 33.8 | 42.5 |
| Ear emergence | 20 | 200 | 75.4 | 34.1 | 43.7 |
| Statistical significance of differences | | | | | |
| All treatments except unfertilized | | | | | |
| Fertilizer | *** | ns | ns | ns | *** |
| 140 kg/ha N in spring vs. top dressings | | | | | |
| Fertilizer | ns | ns | ns | ns | *** |
| Time of application | * | ns | ns | ns | * |
| Fertilizer * time of appl. | ns | ns | ns | ns | ns |
| Top dressings only | | | | | |
| Fertilizer | ns | ns | ns | ns | ** |
| Time of application | * | ns | ns | ns | * |
| Fertilizer * time of appl. | ns | ns | ns | ns | ns |

Table 13. The effect of top dressing of nitrogen on protein content of the flour, loaf volume and rheological properties of the dough in 1988 and 1989.

| Fertilizer application | Flour protein content % | Loaf volume $cm^3$ | Farinograph | | | Extensograph | | |
|---|---|---|---|---|---|---|---|---|
| | | | Water absorption % | Development time min | Stability min | Energy $cm^2$ | Resistence BU | Extensibility mm |
| Unfertilized | 11.9 | 1444 | 52.4 | 2.9 | 4.4 | 74 | 225 | 181 |
| 100 kg/ha N in spring | 13.4 | 1487 | 55.1 | 4.2 | 5.2 | 81 | 206 | 197 |
| 140 kg/ha n in spring | 14.7 | 1528 | 56.4 | 4.8 | 5.1 | 100 | 222 | 214 |
| 140 kg/ha N in spring + CCC | 14.7 | 1542 | 55.6 | 4.6 | 4.9 | 97 | 218 | 216 |
| 100 » + 40 kg/ha N as CAN, tillering | 14.9 | 1525 | 56.4 | 5.0 | 5.5 | 96 | 210 | 213 |
| 100 » » ear emergence | 15.2 | 1544 | 57.4 | 5.0 | 6.1 | 95 | 202 | 219 |
| 100 » + 40 kg/ha N as CN, tillering | 15.7 | 1556 | 57.0 | 5.2 | 6.0 | 107 | 221 | 219 |
| 100 » » ear emergence | 15.6 | 1537 | 58.0 | 5.2 | 5.8 | 109 | 224 | 224 |
| 100 » + 40 kg/ha N as urea, ganular, tillering | 15.0 | 1503 | 56.9 | 5.0 | 6.1 | 109 | 239 | 216 |
| 100 » » » » ear emergence | 15.1 | 1553 | 56.6 | 5.2 | 5.6 | 104 | 214 | 224 |
| 100 » + 40 kg/ha N as urea, foliar, tillering | 14.5 | 1522 | 56.5 | 4.7 | 5.7 | 105 | 216 | 218 |
| 100 » » » » ear emergence | 14.8 | 1527 | 56.3 | 4.9 | 5.0 | 96 | 208 | 213 |
| Fertilizers for top dressing | | | | | | | | |
| CAN | 15.1 | 1534 | 56.9 | 5.0 | 5.8 | 96 | 206 | 216 |
| CN | 15.6 | 1546 | 57.5 | 5.2 | 5.9 | 108 | 222 | 222 |
| Urea, granular | 15.1 | 1528 | 56.7 | 5.1 | 5.9 | 106 | 226 | 220 |
| Urea, foliar application | 14.6 | 1524 | 56.4 | 4.8 | 5.4 | 101 | 212 | 215 |
| Times of application of top dressing | | | | | | | | |
| Tillering | 15.0 | 1526 | 56.9 | 5.0 | 5.8 | 104 | 222 | 216 |
| Ear emergence | 15.2 | 1540 | 57.1 | 5.1 | 5.6 | 101 | 212 | 220 |
| Statistical significance of differences | | | | | | | | |
| All treatments except unfertilized | | | | | | | | |
| Fertilizer | *** | ns | *** | *** | ns | ns | ns | *** |
| 140 kg/ha N in spring vs. top dressings | | | | | | | | |
| Fertilizer | * | ns | ns | ns | ns | ns | ns | ns |
| Time of application | ns | ns | ns | ns | ns | ns | ns | ns |
| Fertilizer * time of application | ns | ns | ns | ns | ns | ns | ns | ns |
| Top dressings only | | | | | | | | |
| Fertilizer | * | ns | ns | ns | ns | ns | ns | ns |
| Time of application | ns | ns | ns | ns | ns | ns | ns | ns |
| Fertilizer * time of application | ns | ns | ns | ns | ns | ns | ns | ns |

low, below 120, to justify a baking test. All the nitrogen applications increased the protein content of the flour statistically significantly compared to the unfertilized treatment (Table 13). However, the loaf volume was not affected statistically significantly. Water absorption, development time and extensibility of the dough were smaller in the unfertilized treatment than in the fertilized treatments. Otherwise, the rheological properties of the dough were not affected by the treatments.

The research material is, however, small in terms of statistical analysis, because the baking tests were made from the pooled yields of replicated plots, and the experiments and varieties were used as replicates. Also the poor yield quality in many of the experimental years limited the material. Severalfold too high dose of ascorbic acid in the recipe for the baking test and the high content of protein in the grain, in general, may have affected the results, too. However, it has been suggested that overdosing ascorbic acid does not affect the result of baking (WOOD 1985).

## 4.3. Discussion

### 4.3.1. Yield, protein content and nitrogen yield

The results of the yield and protein content in these experiments agree with the results of previous Finnish experiments on the subject. If we compare the corresponding amounts of nitrogen given at sowing and partly given as top dressing during the growing season, the protein content of the grain is increased, but the yield is decreased by top dressing (KONTTURI 1977, 1982a and b, KONTTURI et al. 1979, KONTTURI and RANTANEN 1986, LAMPINEN 1975, 1977, 1979 and 1989).

In Sweden, MATTSON (1984) noticed no difference in the yield or protein content of the grain when nitrogen was applied to winter wheat in spring or at different growth stages during the growing season. BENGTSSON (1989) showed that application of part of the nitrogen by top dressing to winter wheat during the growing season compared to spring application did not affect the yield, but increased protein content of the grain by 0.1—0.2 percentage units. In Norway, STABBETORP (1989) noticed that top dressing part of the 140 kg/ha dose to spring wheat increased the yield by about 3 % and the protein content by 0.4 percentage units compared to a single dressing at sowing.

A great proportion of the experiments in other countries, e.g. in the United Kingdom, on winter wheat show that spring application compared to an equal amount of nitrogen given at ear emergence results in a higher yield and a lower protein content (DAMPNEY 1987, MCCLEAN 1987).

Some more encouraging results have been obtained for top dressing, both in Finland and in other countries but in these experiments top dressing of nitrogen has been compared only with a basic fertilizer given at sowing. So the amount of nitrogen applied has not been equal (FINNEY et al. 1957, RAININKO 1966, TALVITIE 1971, SALONEN and LARPES 1972, PELTONEN 1991). The same conclusion can be drawn on the basis of the results of the present investigation if top dressings are compared with the application of 100 kg/ha nitrogen at sowing.

The different forms of nitrogen used for top dressing have previously been compared in Finland by RAININKO (1966) and LAMPINEN (1975). RAININKO (1966) did not find any difference between granular calcium nitrate and foliar urea in their effect on the protein content of spring

wheat. LAMPINEN (1975) noticed that urea, both sprayed and applied granular, resulted in a lower protein content compared to granular calcium nitrate application. FAJERSSON (1961), in Sweden, and COOPER and BLAKENEY (1990), in Australia, obtained similar results. SVENSSON and LINDAHL (1989), in Sweden, obtained similar results in two out of four trials. The results of the present investigation are equal to most of the above mentioned investigations when foliar-applied urea is compared with the other three treatments.

LAMPINEN (1975) suggested that the lower protein content by foliar urea is caused by the volatilization of ammonia released from urea in the soil. Part of the sprayed urea ends up on the soil surface, especially when applied in the early growing season. Although the Finnish soils are quite acid and the potential for volatilization of ammonia is low (NISKANEN et al. 1990), it can partly explain the difference in the nitrogen yield of about 3 kg/ha between urea and calcium nitrate which, however, is not statistically significant. Another more probable explanation is that the ammonium nitrogen released from urea is immobilized to a greater extent than nitrate nitrogen as shown e.g. by NIELSEN and JENSEN (1986), RECOUS et al. (1988a) and RIGA et al. (1988).

One explanation for the lower protein content and nitrogen yield from urea spraying can be volatilization of nitrogen from the leaves of the plants after it has been taken up and metabolized to ammonia and $CO_2$ (VASILAS et al. 1980). This conclusion is supported by scorching of the leaves observed in some years after urea spraying. The phenomenon is assumed to be caused by phytotoxicity of ammonia (VASILAS 1980) or rather urea (KROGEMEIER et al. 1989), not by osmotic effects as often assumed.

In agreement with the results of the present investigation, also LAMPINEN (1975) and TEITTINEN (1975) showed that growth regulator treatment with chlormequatchloride decreased the protein content by increasing the yield. The decrease observed by TEITTINEN (1975) was 0.3 percentage units, which is the same as indicated in the present study. In Sweden, BENGTSSON (1987) noticed a decrease 0.2 percentage units in protein content in experiments with two varieties and three nitrogen doses, and using chlormequatchloride as growth regulator. These results show that it is not the growth regulator, but the dilution of the protein content by higher yield of carbohydrates that causes the decrease in protein content.

Many of the results from the field experiments do not support the theory that both yield and protein content are increased by top dressing part of the nitrogen dose during the growing season. E.g. none of the 16 cases of experiments and varieties in these experiments support this theory. So it is reasonable to speculate the reasons for this contradiction.

Experiments made in controlled environments show that the photosynthesis of the plants is greatly dependent on the nitrogen nutrition and that when the nitrogen concentration of a leaf decreases the amount of photosynthesis is decreased (NATR 1972). SPIERTZ and ELLEN (1978) showed in field experiments that nitrogen application to winter wheat at anthesis may delay the senescence of the leaves and prolong the photosynthesis in the plants, which increases yield. LAWLOR et al. (1989) showed that winter wheat given no nitrogen fertilizer senesced and its photosynthesis was ceased one week earlier than a crop given 200 kg/ha nitrogen.

It has also been shown that the interruption of nitrogen uptake by the plant, e.g. because of drought or low nitrogen content of soil, may lead to earlier translocation of nitrogen from the leaves, causing a reduction in the photosynthesis and in the yield (GREGORY et al. 1979). There are, however, exceptions where nitrogen did not increase photosynthesis (THOMAS and THORNE 1975).

According to GREGORY et al. (1981), top

dressing of nitrogen increased the nitrogen uptake by plants. The nitrogen was translocated to the grain later in the plants top dressed with nitrogen than in plants given no top dressing. At harvest the amounts of nitrogen translocated from the leaves and straw were, however, almost equal in both treatments. The maximal photosynthesis of the flag leaf was not depending on nitrogen application. They concluded that many of the results of the plant physiological studies showing a positive influence of the nitrogen concentration on the photosynthesis of the leaf (NATR 1972, OSMAN et al. 1977), have been obtained in as low nitrate concentration of the nutrient solution as $10^{-5}$ M, while a typical nitrate concentration in the soil solution is about $10^{-3}$ M. So, in many of the agricultural soils the nitrate concentration is not low enough to reduce the photosynthesis and yield remarkably.

According to the literature it is obvious that splitting the nitrogen application partly to the growing season does not affect the nitrogen nutrition of the grain filling period of a crop to an extent that would increase yield. The slight increase in the protein content of the grain yield was a consequence of yield reduction and the enrichment of the nitrogen content of the grain, for the nitrogen yields of the treatments were almost equal and the differences in them were not statistically significant. A plant physiological study to confirm these assumptions was, however, outside the scope of the present investigation.

### 4.3.2. Lodging, falling number, test weight, thousand grain weight and wet gluten

The results of lodging agree with the results of LAMPINEN (1989). KONTTURI (1982b) noticed that the lodging of barley, which generally has weaker straw than wheat, was more pronouncedly affected by the time of nitrogen application. Delaying nitrogen application thus seems to have a tendency towards reducing lodging of the crops. This phenomenon does not, however, have any great practical meaning, because the reduction is so small.

Falling number was not affected by splitting the fertilizer application. However, it tended to be higher on the treatments where lodging was decreased as noticed by LAMPINEN (1989).

In agreement with the results of the present study, test weight and thousand grain weight have not previously been noticed to be affected by the time of application or by the form of nitrogen fertilizer (FINNEY et al. 1957, TIPPLES et al 1977). The principle of top dressing part of the nitrogen late in the growing season is, however, based on the observation that it increases grain size (DARWINKEL 1983). In the present study, in agreement with previous studies (DUBETZ et al. 1979, DOEKES and WENNEKES 1982), the gluten content of the flour correlated with the protein content of the grain.

### 4.3.3. Baking quality

FINNEY et al. (1957) noticed that the protein content of the grain could be increased remarkably by urea spraying of the crops, but increasing protein contents by repeated late sprayings did not improve the baking quality of the grain. The amount of water-soluble nitrogen compounds was greater in the samples where the baking quality was poorer than expected. They concluded that this was a consequence of incomplete synthesis of gluten proteins. COOPER and BLAKENEY (1990) and RANDALL et al. (1990) could not show a corresponding decrease in the baking quality of the proteins by urea spraying at anthesis or at ear emergence. They concluded that the difference in their results compared to the results of FINNEY et al. (1957) was due to the smaller range of protein levels in their results.

According to PUSHMAN and BINGHAM (1976), granular nitrogen fertilizer increased the loaf volume of winter wheat, while additional late

urea spraying did not, although the protein content was increased more by the late spraying alone than by the granular fertilizer alone. They concluded that the nitrogen applications after anthesis occur too late to improve the baking quality of wheat.

TIPPLES et al. (1977) observed that the high protein content produced by urea sprayings alone resulted in a weaker dough compared to corresponding protein contents produced by other nitrogen fertilizers. The extensogram height was lower, mixing times were shorter, and the bread crumb texture was deteriorated. On the other hand, the baking quality of the high protein wheat produced both by urea spraying and granular fertilizer was better than the baking quality of wheat applied granular fertilizer alone.

GOODING et al. (1987) showed that urea spraying at the flag leaf stage or at ear emergence resulted in poorer baking quality of the protein when given with fungicide treatment, but not without it. GRIFFITHS et al. (1987) noticed that an increase in the protein content obtained by urea spraying at ear emergence did not increase the loaf volume of wheat.

In a series of experiments made on 12 sites in the United Kingdom, the loaf volume increased with increasing grain protein content only at one site; it was not affected at nine sites and it was decreased at two sites (SYLVESTER-BRADLEY 1990). Any indication of poorer quality of protein produced by urea spraying compared to application of granular fertilizer could not be shown. It was concluded that the result may be a consequence of high protein contents in the experiments in general. SALMON et al. (1990), on the other hand, noticed that late urea sprayings increased the level of protein in grain and the baking quality of the protein more than granular fertilizer application, probably because of better recovery of the foliar application of urea nitrogen.

The tests of the Research Laboratory of Finnish Grain Board also showed in some cases softening of the gluten in samples by top dressing of nitrogen as urea spraying when wheat was given a 40 kg/ha dressing of nitrogen in addition to 80 or 120 kg/ha basic application at sowing (HEIMONEN-KAUPPI et al. 1987).

MCNEAL et al. (1963) showed that granular nitrogen 50—200 kg/ha applied in one dose, either at sowing or at anthesis, resulted in the same protein content at respective fertilizer levels. As a consequence of the late nitrogen application the valorimetric value of the dough was statistically significantly smaller. Also the loaf volume was smaller, although this difference was not statistically significant.

A change in the nitrogen/sulphur ratio in the grain has been suggested to be the reason for the decrease in the baking quality produced by late nitrogen application and especially by late urea spraying (GOODING et al. 1987). Sulphur deficiency has been noticed to decrease the contents of sulphur containing amino acids and the proteins producing disulphide bonds in the grain. This leads to changes similar to those observed in connection with the poor baking quality of the wheat protein (BYERS and BOLTON 1979, WRIGLEY et al. 1984, BYERS et al. 1987). Also the amounts of the amino acids asparagine and arginine, and the proteins of low sulphur omega-gliadins increased with decreasing amounts of the sulphur containing proteins of the alfa-, beta- and gamma-gliadins.

TIMMS et al. (1981) showed that high nitrogen content in the plant increased the N/S ratio in the grain. It caused similar changes in the proteins of the grain as a consequence of late urea sprayings as sulphur deficiency throughout the whole growing season in the above referred pot experiments.

However, the loaf volume of wheat has not been increased by combined sulphur-urea spraying (GRIFFITHS et al. 1987, GRIFFITS et al. 1990), by sulphur spraying alone (LEGRIS-DELAPORTE and LANDRY 1987), or by granular sulphur-nitrogen application at ear emergence (RANDALL et al. 1990). DAMPNEY and SALMON

(1990) noticed no or only a small influence of micronized elementary sulphur spraying on the N/S ratio in the grain, although this ratio was critically high. SALMON et al. (1990) showed that micronized sulphur spraying slightly reduced the proportion of the urea induced low quality omega-gliadins.

RANDALL et al. (1990) observed that sulphur application increased the sulphur concentration in the leaves and stems of the crops, but not that of the grain. Late nitrogen application, however, increased also the sulphur concentration of the grain. They concluded that the role of sulphur deficiency in the reduction of baking quality of proteins produced by late applications of nitrogen still remains an open question. LEGRIS-DELAPORTE et al. (1987) noticed that in wheat plants the micronized elemental sulphur applied on the leaves is oxidized to sulphate ions and concluded that the additional sulphur in the plant is thus detoxified and would be stored in the cells and not completely metabolized.

The top dressings of nitrogen at ear emergence did not in the present study decrease the baking quality measured by the loaf volume or by some rheological properties of the dough. According to the literature presented above it is obvious that the decreasing of baking quality by urea spraying or late nitrogen application in general will probably show more clearly by considerably later applications of nitrogen and also probably when larger amounts of nitrogen are used for the late application. The reason for this deteoriation in dough properties may be connected with the N/S ratio in the grain. It can also be concluded from the literature that the decrease in baking quality by late applications is connected e.g. with certain weather conditions that are not yet fully understood (e.g. SVENSSON and LINDAHL 1989).

## 5. THE EFFECT OF TIME OF APPLICATION AND THE FORM OF NITROGEN ON THE FATE OF $^{15}$N-LABELLED FERTILIZER IN THE SOIL-PLANT SYSTEM AND IN THE PROTEIN FRACTIONS OF THE GRAIN

### 5.1. Introduction

Split application of nitrogen to a cereal crop is occasionally suggested to increase the protein content of the grain. The method is also suggested to improve the recovery of the fertilizer and thus to decrease the environmental pollution caused by nitrogen.

Top dressing part of the nitrogen dose may, however, have some disadvantages. Fertilizer placement cannot be applied to top dressing of fertilizer. This technique, which is widely accepted by the farmers in Finland, improves especially the availability of nitrogen (AURA 1967, ESALA and LARPES 1984a). Some years may be so dry that the top dressed fertilizer is not translocated from the top of the soil to the plant roots, especially on clay soils that are typical in spring wheat cultivation in Southern Finland (KAILA and HÄNNINEN 1961, NIEMINEN et al. 1967). This observation of poor movement of the fertilizer nitrogen broadcasted on the soil surface to the plant roots led to the development and breakthrough of the fertilizer placement technique in Finland in the 1960s (ELONEN 1980).

Nitrogen fertilizer applied at different times of the growing season can also be assumed, besides affecting the quality of protein, to be deposited to the different proteins of the grain, if these proteins are formed at different stages of grain development.

All these matters can be studied using $^{15}$N-labelled fertilizers. Only some basic questions

can be studied in pot experiments, but total balances of the fertilizer nitrogen require field experiments despite the high cost of $^{15}N$-labelled fertilizer. Unconfined microplots provide the most suitable and close to nature compromise between reducing the costs of the fertilizer and getting reliable information on the fate of fertilizer nitrogen in field conditions (SAFFIGNA 1987).

Pot experiments investigating a crop's ability to take up $^{15}N$-labelled fertilizer nitrogen in optimal conditions and its fate in the soil-plant system were conducted in 1985. Field experiments to investigate the same subject in field conditions were conducted in 1987—1990.

## 5.2. Results from the pot experiment

The two varieties Luja and Kadett did not differ in the pot experiment in their reactions to the time of application of fertilizer in terms of yield, nitrogen content and recovery of $^{15}N$-labelled fertilizer in the different parts of the soil-plant system, i.e. the interaction of the variety and the application time on these characters was not statistically significant. The results of the two varieties have thus been treated together in the following presentation.

### 5.2.1. Yield and protein content

Only the top dressing of nitrogen at sowing increased the grain yield of wheat statistically significantly compared to the basic application (Appendix 5). The grain yield was about 35 % of the total dry matter biomass of the plants. The straw yields were about 50 %, those of chaff 10 % and roots 6 % of the total dry matter biomass of the plants.

The nitrogen content of the straw was about one fifth of that of the grain (Appendix 5). The nitrogen content of the roots was about 2.5 times that of straw and about half that of the grain. The nitrogen (and protein) content of grain was generally higher the later the fertilizer application. There was a statistically significant difference only between the application at sowing and the application two weeks after ear emergence. Also all the top dressed crops had a statistically significantly higher protein content than the crops only receiving the basic fertilizer dose at sowing.

### 5.2.2. Recovery of $^{15}N$-labelled fertilizer in the different plant parts and soil, and the losses of fertilizer nitrogen

Of the total nitrogen in the soil-plant system (about 6300 mg, Appendix 5), about 79 % was in the soil and 21 % in the plants. About 70 % of the plant nitrogen was in the grain, 20 % in the straw, 4 % in the chaff and 6 % in the roots.

The recovery of $^{15}N$-labelled fertilizer nitrogen in the grain was 50.9—70.6 % (Fig. 12, Appendix 5). The recovery was lowest from the application at sowing and highest from the application at the flag leaf stage of the crops. The recovery of $^{15}N$-labelled fertilizer increased gradually when the fertilizer application was delayed until the flag leaf stage and declined thereafter. The lower yield of the variety Kadett explains the lower recovery from the application at the beginning of stem elongation. This phenomenon was not statistically significant.

The pattern of the recovery of $^{15}N$-labelled fertilizer in the grain was similar to that in the whole plant. The recoveries in the whole plants at harvest were 71.6—87.7 %. The recovery of $^{15}N$-labelled nitrogen was highest from the applications at flag leaf stage.

The lower recovery of fertilizer nitrogen from the earlier applications in grain was cor-

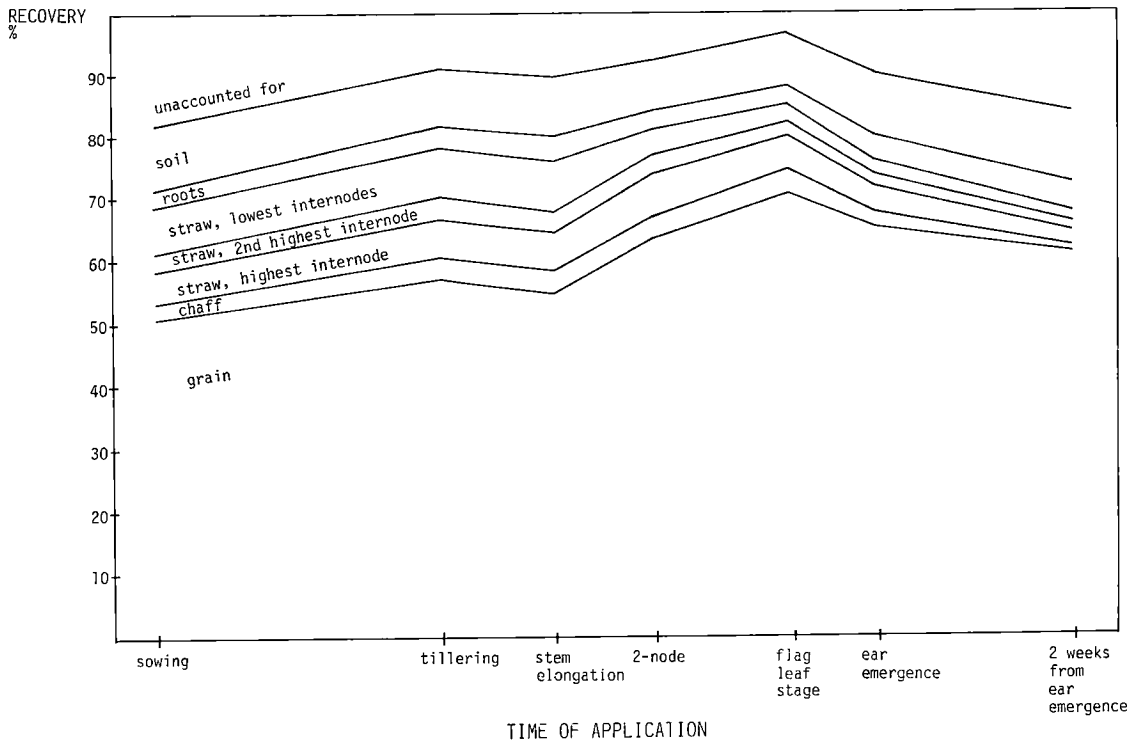



Fig. 12. The effect of time of application on the recovery of $^{15}N$-labelled fertilizer nitrogen in the different plant parts and soil in the pot experiment at harvest. The scale for the time of application is proportional to the time in days between the treatments.

related with a higher recovery in straw and soil and slightly higher losses. Similarly a higher proportion of the later applied $^{15}N$ was recovered in the soil and partly in the roots. Also the losses were higher from the later applications compared to the applications at the flag leaf stage.

The later the time of application, the smaller was the proportion of fertilizer nitrogen recovered in straw, especially in those internodes that were fully developed by the time of fertilizer application. An exception to this rule were the applications made before stem elongation, where the fertilizer recovery first increased as the application was delayed. The phenomenon was especially clear in the lowest internodes: from the applications after the 2-node stage a clearly smaller proportion of fertilizer nitrogen was recovered in this plant part than from the earlier applications. Only about one third of the amount recovered in straw from the application at tillering was recovered in straw from the latest applications.

The recovery of fertilizer nitrogen in the roots was 2—5 %, recovery being generally the higher the later the application. The applications at the 2-node and flag leaf stages were exceptions to this trend. The recoveries from these applications were lower than the trend.

### 5.2.3. Protein fractions in the grain and $^{15}N$-labelled nitrogen in the fractions

Proteins of the grain were fractionated only from four treatments, i.e. sowing, tillering, flag

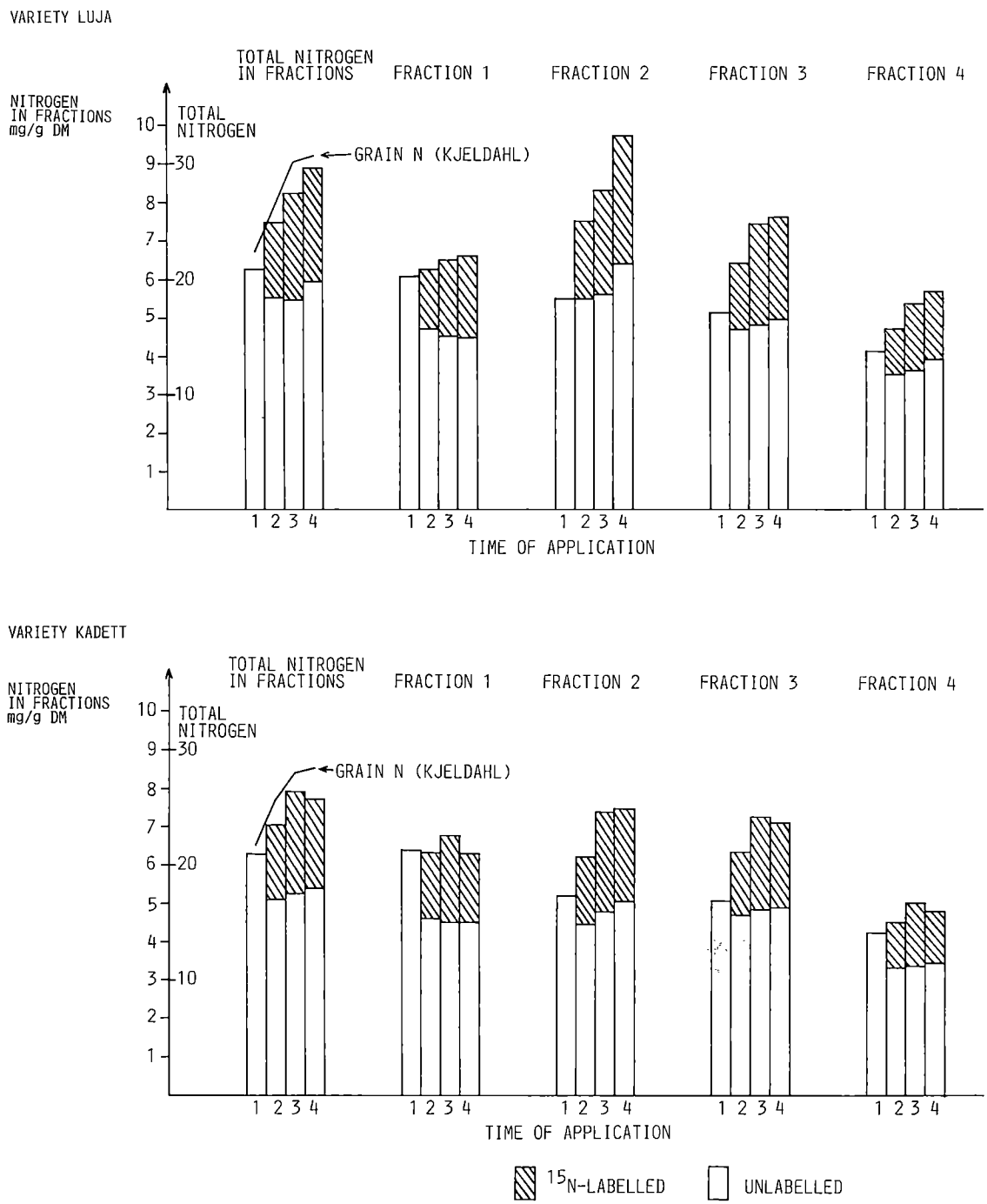



Fig. 13. The effect of time of application of nitrogen fertilizer on amount of nitrogen in the protein fractions soluble in salt solution (fraction 1), aqueous ethanol (fraction 2), aqueous propanol — dilute acetic acid — mercaptoethanol (fraction 3), the insoluble residue (fraction 4) and the sum of the fractions and on the amount of $^{15}N$-labelled nitrogen in the fractions in the pot experiment. Varieties Luja and Kadett. Times of application:
1 = no fertilizer top dressing,
2 = sowing,
3 = flag leaf stage,
4 = two weeks from ear emergence.

leaf stage and two weeks from ear emergence. On average, 92.9 % of the total nitrogen determined by the Kjeldahl method was recovered by the fractionation procedure. The correlation between the two methods was quite good, 0.9269***. The corresponding figures for the $^{15}$N-labelled fertilizer were 84.7 % and 0.8528***, respectively. The interaction between the varieties and the times of fertilizer application was in some cases statistically significant. So, in the following presentation the varieties are treated separately.

The increased nitrogen content in the grain was most profoundly found in the fractions 2, 3 and 4 in that descending order (Fig. 13). This phenomenon was more obvious in Luja than in Kadett. There was almost no effect of fertilizer application and the time of application on the nitrogen content in fraction 1.

The percentage of $^{15}$N-labelled nitrogen in a certain fraction of the total labelled nitrogen in the grain was equal to the corresponding percentage of total nitrogen in the fraction of the total nitrogen in the grain (Table 14). Almost all the increase of nitrogen in fractions 2 and 3 could be recovered as $^{15}$N-labelled nitrogen, especially in fraction 2 of Luja.

The ratio between the fractions 2 and 3 was slightly, but not statistically significantly increased by delaying fertilizer application (Table 15). This phenomenon was equal for both the total and $^{15}$N-labelled nitrogen.

The amount of non-protein nitrogen in the grain was about 2 mg/g DM and it was about 7—9% of the total nitrogen in the grain and about 30 % of the protein nitrogen in fraction 1 (Fig. 14). The corresponding proportions for the $^{15}$N-labelled nitrogen were slightly less,

Table 14. The effect of time of application of nitrogen fertilizer on the proportional amounts of nitrogen and $^{15}$N-labelled nitrogen in the grain in the pot experiment. The results within the same fraction and same column followed by the same letter do not differ statistically significantly according to the Tukey's test (P = 0.05)

| Fraction/ Time of application | Luja | | | Kadett | | |
|---|---|---|---|---|---|---|
| | Nitrogen % of total nitrogen in grain | $^{15}$N-lab. N % of $^{15}$N-lab. nitrogen in grain | $^{15}$N-lab. N % of total N in fraction | Nitrogen % of total nitrogen in grain | $^{15}$N-lab. N % of $^{15}$N-lab. nitrogen in grain | $^{15}$N-lab. N % of total N in fraction |
| FRACTION 1 | | | | | | |
| no top dressing | 29$^{a}$ | | | 31$^{a}$ | | |
| sowing | 25$^{b}$ | 25$^{a}$ | 26$^{b}$ | 27$^{b}$ | 27$^{a}$ | 27$^{b}$ |
| flag leaf stage | 24$^{bc}$ | 23$^{a}$ | 32$^{a}$ | 26$^{b}$ | 25$^{ab}$ | 33$^{a}$ |
| 2 wk from ear emergence | 22$^{c}$ | 20$^{b}$ | 30$^{a}$ | 25$^{b}$ | 23$^{b}$ | 29$^{b}$ |
| FRACTION 2 | | | | | | |
| no top dressing | 26$^{b}$ | | | 25$^{b}$ | | |
| sowing | 30$^{ab}$ | 30$^{b}$ | 26$^{b}$ | 27$^{ab}$ | 27$^{a}$ | 28$^{c}$ |
| flag leaf stage | 30$^{ab}$ | 30$^{b}$ | 33$^{a}$ | 28$^{a}$ | 29$^{b}$ | 35$^{a}$ |
| 2 wk from ear emergence | 32$^{a}$ | 34$^{a}$ | 34$^{a}$ | 29$^{a}$ | 31$^{c}$ | 33$^{b}$ |
| FRACTION 3 | | | | | | |
| no top dressing | 25$^{a}$ | | | 24$^{b}$ | | |
| sowing | 26$^{a}$ | 27$^{a}$ | 27$^{b}$ | 27$^{a}$ | 27$^{a}$ | 26$^{c}$ |
| flag leaf stage | 26$^{a}$ | 28$^{a}$ | 35$^{a}$ | 27$^{a}$ | 27$^{a}$ | 33$^{a}$ |
| 2 wk from ear emergence | 27$^{a}$ | 27$^{a}$ | 35$^{a}$ | 28$^{a}$ | 28$^{a}$ | 30$^{b}$ |
| FRACTION 4 | | | | | | |
| no top dressing | 20$^{a}$ | | | 20$^{a}$ | | |
| sowing | 19$^{a}$ | 18$^{a}$ | 26$^{b}$ | 19$^{b}$ | 18$^{a}$ | 26$^{c}$ |
| flag leaf stage | 20$^{a}$ | 19$^{a}$ | 33$^{a}$ | 19$^{b}$ | 19$^{a}$ | 33$^{a}$ |
| 2 wk from ear emergence | 19$^{a}$ | 18$^{a}$ | 31$^{a}$ | 19$^{b}$ | 17$^{b}$ | 28$^{b}$ |

5—8 % and 22—28 %, respectively (Table 16). About 22—28 % of the non-protein nitrogen was $^{15}$N-labelled fertilizer nitrogen.

There was no statistically significant effect of the time of application on the content of non-protein nitrogen and on the amount of $^{15}$N-labelled non-protein nitrogen in the grain of Luja (Table 16). The proportion of non-protein nitrogen and $^{15}$N-labelled nitrogen from the grain nitrogen and from the grain $^{15}$N-labelled nitrogen was slightly, and for Kadett statistically significantly less for the later application. Also the proportion of $^{15}$N-labelled non-protein nitrogen from the fraction 1 $^{15}$N-labelled nitrogen was statistically significantly less from the later application in Kadett. The proportion of $^{15}$N-labelled nitrogen from the non-protein nitrogen was statistically significantly higher from the application at the flag leaf stage. These

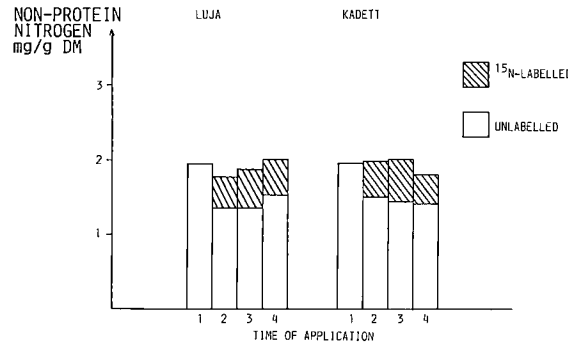



Fig. 14. The effect of time of application of nitrogen on the content of non-protein nitrogen in the grain and on the amount of $^{15}$N-labelled nitrogen in the non-protein nitrogen in the pot experiment. Times of application as in figure 13.

Table 15. The effect of time of application of nitrogen fertilizer on the ratio of nitrogen and $^{15}$N-labelled nitrogen in the grain protein fractions 2 and 3. The results within the same column followed by the same letter do not differ statistically significantly according to the Tukey's test (P = 0,05)

| Time of application | Luja | | Kadett | |
|---|---|---|---|---|
| | 2/3-ratio total N | 2/3-ratio $^{15}$N-lab. N | 2/3-ratio total N | 2/3-ratio $^{15}$N-lab. N |
| No top dressing | 1.07$^{a}$ | | 1.02$^{a}$ | |
| Sowing | 1.18$^{a}$ | 1.12$^{a}$ | 0.98$^{a}$ | 1.04$^{a}$ |
| Flag leaf stage | 1.13$^{a}$ | 1.07$^{a}$ | 1.01$^{a}$ | 1.06$^{a}$ |
| 2 wk from ear emergence | 1.28$^{a}$ | 1.26$^{a}$ | 1.05$^{a}$ | 1.12$^{a}$ |

Table 16. The effect of time of application of nitrogen fertilizer on the proportional amounts of non-protein nitrogen and $^{15}$N-labelled non-protein nitrogen in the grain in the pot experiment. The results within the same fraction and same column followed by the same letter do not differ statistically significantly according to the Tukey's test (P = 0.05)

| Time of application | Nitrogen % of total N in grain | Nitrogen % of N in fraction 1 | $^{15}$N-lab. N % of $^{15}$N-lab. N in grain | $^{15}$N-lab. % of $^{15}$N-lab. N in fraction 1 | $^{15}$N-lab. N % of non-protein N |
|---|---|---|---|---|---|
| Variety Luja | | | | | |
| No top dressing | 9.4$^{a}$ | 32$^{a}$ | | | |
| Sowing | 7.3$^{ab}$ | 29$^{a}$ | 6.4$^{a}$ | 26$^{a}$ | 23$^{b}$ |
| Flag leaf stage | 6.9$^{b}$ | 29$^{a}$ | 5.8$^{a}$ | 25$^{a}$ | 28$^{a}$ |
| 2 wk from ear emergence | 6.8$^{b}$ | 31$^{a}$ | 4.8$^{a}$ | 24$^{a}$ | 23$^{b}$ |
| Variety Kadett | | | | | |
| No top dressing | 9.4$^{a}$ | 31$^{a}$ | | | |
| Sowing | 8.6$^{ab}$ | 32$^{a}$ | 7.7$^{a}$ | 28$^{a}$ | 24$^{a}$ |
| Flag leaf stage | 7.7$^{bc}$ | 30$^{a}$ | 6.5$^{b}$ | 26$^{ab}$ | 28$^{b}$ |
| 2 wk from ear emergence | 7.1$^{c}$ | 29$^{a}$ | 5.2$^{c}$ | 22$^{b}$ | 22$^{c}$ |

differences reflect the proportions of total nitrogen in the fractions more than any other important phenomenon in the physiology of the plant or the baking quality of the flour.

## 5.3. Results from the field experiment

### 5.3.1. Yield, protein content and nitrogen uptake

The grain yields were highest in 1990, almost as high in 1987 and considerably lower in 1988 and 1989 in the field experiment using $^{15}$N-labelled fertilizer (Table 17). The straw yield was exceptionally high in the cool and rainy year of 1987, close to 'normal' in 1990 and low in 1988 and 1989. Nitrogen uptake of the crops was highest in 1990 and lowest in 1988. The protein contents were high, especially in 1989,

Table 17. The effect of fertilizer and time of application of fertilizer as top dressing to spring wheat on the dry matter, and nitrogen yield and protein content in the experiments with $^{15}$N-labelled fertilizer (= *) in 1987—1990. The results within the same year and the same column followed by the same letter do not differ significantly according to the Tukey's test (P = 0.05).

| Fertilizer application | Yield kg/ha 85 % DM | Protein content % | Straw yield kg/ha DM | Nitrogen yield kg/ha | | |
|---|---|---|---|---|---|---|
| | | | | Grain | Straw + chaff | Grain + straw + chaff |
| 1987 | | | | | | |
| Unfertilized | 1580$^{b}$ | 9.1$^{c}$ | 2910$^{c}$ | 21.4$^{c}$ | 12.5$^{d}$ | 34.0$^{d}$ |
| 100 kg/ha N spring | 2930$^{a}$ | 9.7$^{bc}$ | 5630$^{b}$ | 42.4$^{b}$ | 29.6$^{c}$ | 72.1$^{c}$ |
| 100 » + 40 N* spring | 3150$^{a}$ | 10.1$^{b}$ | 6180$^{ab}$ | 47.4$^{ab}$ | 38.0$^{bc}$ | 85.4$^{bc}$ |
| 100 » + 40 N* tillering | 3160$^{a}$ | 10.8$^{a}$ | 6380$^{a}$ | 50.8$^{a}$ | 48.6$^{ab}$ | 99.4$^{ab}$ |
| 100 » + 40 N* ear emergence | 3150$^{a}$ | 11.1$^{a}$ | 6210$^{ab}$ | 52.1$^{a}$ | 54.0$^{a}$ | 106.0$^{a}$ |
| 100 » + 20 N* + 20 N | 3060$^{a}$ | 10.9$^{a}$ | 6350$^{a}$ | 49.9$^{ab}$ | 53.5$^{a}$ | 103.4$^{a}$ |
| 100 » + 20 N + 20N* | 3130$^{a}$ | 11.0$^{a}$ | 5820$^{ab}$ | 51.3$^{a}$ | 47.0$^{ab}$ | 98.3$^{ab}$ |
| 1988 | | | | | | |
| Unfertilized | 1340$^{b}$ | 13.1$^{b}$ | 1140$^{b}$ | 25.9$^{b}$ | 5.8$^{b}$ | 31.7$^{b}$ |
| 100 kg/ha N spring | 2660$^{a}$ | 15.7$^{a}$ | 2200$^{a}$ | 62.5$^{a}$ | 14.0$^{a}$ | 76.5$^{a}$ |
| 100 » + 40 N* spring | 2220$^{a}$ | 16.7$^{a}$ | 1910$^{a}$ | 55.3$^{a}$ | 14.1$^{a}$ | 69.4$^{a}$ |
| 100 » + 40 N* tillering | 2460$^{a}$ | 16.4$^{a}$ | 2000$^{a}$ | 60.2$^{a}$ | 14.0$^{a}$ | 74.2$^{a}$ |
| 100 » + 40 N* ear emergence | 2270$^{a}$ | 16.2$^{a}$ | 1890$^{a}$ | 54.8$^{a}$ | 12.6$^{a}$ | 67.4$^{a}$ |
| 100 » + 20 N* + 20N | 2470$^{a}$ | 16.4$^{a}$ | 2000$^{a}$ | 60.3$^{a}$ | 12.9$^{a}$ | 73.1$^{a}$ |
| 100 » + 20 N + 20 N* | 2460$^{a}$ | 16.4$^{a}$ | 2030$^{a}$ | 59.9$^{a}$ | 13.9$^{a}$ | 73.8$^{a}$ |
| 1989 | | | | | | |
| Unfertilized | 1620$^{b}$ | 14.2$^{b}$ | 920$^{c}$ | 34.4$^{b}$ | 9.7$^{c}$ | 44.2$^{c}$ |
| 100 kg/ha N spring | 2450$^{a}$ | 18.7$^{a}$ | 1540$^{b}$ | 68.3$^{a}$ | 28.4$^{b}$ | 96.7$^{ab}$ |
| 100 » + 40 N* spring | 2970$^{a}$ | 18.3$^{a}$ | 2000$^{a}$ | 81.1$^{a}$ | 39.1$^{a}$ | 120.2$^{a}$ |
| 100 » + 40 N* tillering | 2310$^{ab}$ | 18.1$^{a}$ | 1490$^{b}$ | 62.4$^{a}$ | 31.9$^{ab}$ | 94.5$^{b}$ |
| 100 » + 40 N* ear emergence | 2450$^{a}$ | 18.7$^{a}$ | 1640$^{b}$ | 68.3$^{a}$ | 33.1$^{ab}$ | 101.5$^{ab}$ |
| 100 » + 40 N* urea tillering | 2450$^{a}$ | 18.0$^{a}$ | 1510$^{b}$ | 65.9$^{a}$ | 27.7$^{b}$ | 93.7$^{b}$ |
| 100 » + 40 N* urea ear emergence | 2380$^{a}$ | 18.6$^{a}$ | 1420$^{b}$ | 66.1$^{a}$ | 27.7$^{b}$ | 93.9$^{b}$ |
| 1990 | | | | | | |
| Unfertilized | 2250$^{b}$ | 13.2$^{b}$ | 1650$^{a}$ | 44.3$^{b}$ | 12.2$^{b}$ | 56.5$^{b}$ |
| 100 kg/ha N spring | 3530$^{a}$ | 16.9$^{a}$ | 2360$^{a}$ | 89.0$^{a}$ | 28.7$^{a}$ | 117.8$^{a}$ |
| 100 » + 40 N* spring | 3340$^{ab}$ | 17.1$^{a}$ | 2290$^{a}$ | 85.0$^{a}$ | 31.8$^{a}$ | 116.8$^{a}$ |
| 100 » + 40 N* tillering | 3570$^{a}$ | 16.8$^{a}$ | 2440$^{a}$ | 89.2$^{a}$ | 30.7$^{a}$ | 119.9$^{a}$ |
| 100 » + 40 N* ear emergence | 3590$^{a}$ | 16.6$^{a}$ | 2620$^{a}$ | 88.7$^{a}$ | 33.0$^{a}$ | 121.7$^{a}$ |
| 100 » + 40 N* urea tillering | 3580$^{a}$ | 16.4$^{a}$ | 2500$^{a}$ | 87.3$^{a}$ | 36.7$^{a}$ | 124.0$^{a}$ |
| 100 » + 40 N* urea ear emergence | 3740$^{a}$ | 16.3$^{a}$ | 2560$^{a}$ | 90.9$^{a}$ | 35.2$^{a}$ | 126.1$^{a}$ |

but also in 1988 and 1990, and low in 1987.

When comparing the treatment applying 100 kg/ha nitrogen with the unfertilized treatment, the grain yield of spring wheat increased by 85 % in 1987, 100 % in 1988, 50 % in 1989 and 57 % in 1990. When comparing the treatments applying 140 kg/ha with the unfertilized plots the yield increases were about 200 %, 66—84 %, 44—83 %, and 48—65 %, respectively.

The yields of the treatments applying 100 or 140 kg/ha nitrogen did not differ statistically significantly. The experiments were arranged on microplots; therefore the variation between the replicates was great and it is difficult to say if even the quite large differences in yields were caused by the variability or by the experimental treatments.

In 1987, the protein content of the grain yield increased by the top dressing treatments compared to the application of the corresponding amount of nitrogen in spring. In 1988, 1989 or 1990 there were no statistically significant differences in protein content between the fertilized treatments.

In all years the protein contents of the fertilized plots, except application of 100 kg/ha nitrogen in spring in 1987, were statistically significantly higher than those of the unfertilized plots.

The results of 1987 correlated quite well with the results of Kadett in the experiment 'Split application of nitrogen fertilizer to spring wheat', which was arranged on larger plots and situated next to the $^{15}N$ experiment on microplots (Appendices 2 and 4). The yields of the $^{15}N$ experiment were 40—80 kg/ha higher and the protein contents were 0.8—1.2 percentage units lower than on the other experiment in question.

In 1988, corresponding yield differences were −480— + 190 kg/ha, and the differences in the protein contents + 0.2— + 1.3 percentage units The results were more contradictory. The experimental plots were situated a little further away from each other in 1988.

In 1989, the results of these experiments were quite different from each other: the yields were about 1500—1700 kg/ha lower and the protein contents 4.3—5.6 % higher and the overall growth was much poorer in the $^{15}N$ experiment than in the experiment 'Split application of nitrogen fertilizer for spring wheat'. The difference was probably a consequence of a crusting shower after the sowing of the $^{15}N$ experiment and the poorer moisture conditions of the exceptionally dry year. In 1990, the larger experiment was no more arranged, so a corresponding comparison is not possible.

Nitrogen fertilizer application increased the nitrogen uptake by the crops statistically significantly in all the experimental years. Especially top dressing of nitrogen at ear emergence increased the nitrogen uptake by the plant in 1987. In 1988 and 1990, there were no statistically significant differences in the nitrogen uptake between the fertilized treatments. In 1989, the spring application of 140 kg/ha nitrogen resulted in the highest nitrogen uptake probably because of an experimental error caused by breaking of the crust by application of the $^{15}N$-labelled fertilizer after sowing, which resulted in better emergence and growth throughout the growing season on these plots.

### 5.3.2. Recovery of $^{15}N$-labelled fertilizer

The recovery of $^{15}N$-labelled fertilizer in the above ground parts of the crop was highest in 1987 and 1990, and lowest in 1988 (Table 18). Favourable moisture conditions resulted in better growth and nitrogen uptake by the crops in 1987 and 1990, whereas drought restricted growth and translocation of nitrogen to the plant roots, especially in 1988, but also in 1989. In 1987, the crops did not fully mature, and the straw yields were high, which resulted in a greater proportion of the nitrogen to be retained in the straw. This reduced the recovery of fertilizer nitrogen in the grain.

Table 18. The effect of nitrogen fertilizer and time of application of nitrogen fertilizer as top dressing to spring wheat on the recovery of $^{15}N$-labelled fertilizer nitrogen (= *) in the soil-plant system at harvest. Results from 1987—1990. The results within the same year and the same column followed by the same letter do not differ statistically significantly according to Tukey's (P = 0.05).

| Fertilizer application | Recovery, % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Grain | Straw + chaff | Grain + straw + chaff | Soil + roots | | | Soil + roots total | Plant + soil | Weeds | Unaccounted for |
| | | | | 0—25 cm | 25—60 cm | 60—90 cm | | | | |
| 1987 | | | | | | | | | | |
| 40 N* spring | 17.7$^{c}$ | 14.6$^{c}$ | 32.3$^{d}$ | 23.8$^{a}$ | 11.4$^{a}$ | 0.0$^{a}$ | 35.2$^{a}$ | 67.5$^{a}$ | — | 32.5$^{a}$ |
| 40 N* tillering | 35.0$^{a}$ | 28.0$^{ab}$ | 63.0$^{ab}$ | 26.0$^{a}$ | 1.1$^{a}$ | 0.4$^{a}$ | 27.5$^{a}$ | 90.5$^{a}$ | — | 9.6$^{a}$ |
| 40 N* ear emergence | 37.1$^{a}$ | 31.6$^{a}$ | 68.7$^{a}$ | 26.7$^{a}$ | 1.5$^{a}$ | 0.6$^{a}$ | 28.9$^{a}$ | 97.6$^{a}$ | — | 2.4$^{a}$ |
| 20 N* + 20 N till. + ear em. | 27.5$^{b}$ | 24.2$^{b}$ | 51.7$^{c}$ | — | — | — | — | — | — | — |
| 20 N + 20 N* till. + ear em. | 33.6$^{a}$ | 25.3$^{ab}$ | 58.9$^{bc}$ | — | — | — | — | — | — | — |
| 1988 | | | | | | | | | | |
| 40 N* spring | 20.0$^{ab}$ | 5.3$^{a}$ | 25.3$^{a}$ | 53.4$^{a}$ | 13.4$^{a}$ | 3.8$^{a}$ | 70.6$^{a}$ | 95.8$^{a}$ | — | 4.1$^{b}$ |
| 40 N* tillering | 17.7$^{ab}$ | 3.5$^{abc}$ | 21.2$^{ab}$ | 47.2$^{a}$ | 9.5$^{a}$ | 1.6$^{a}$ | 58.3$^{ab}$ | 79.5$^{ab}$ | — | 20.5$^{ab}$ |
| 40 N* ear emergence | 12.6$^{b}$ | 1.9$^{c}$ | 14.6$^{b}$ | 34.7$^{a}$ | 13.0$^{a}$ | 1.6$^{a}$ | 49.3$^{b}$ | 63.9$^{b}$ | — | 36.1$^{a}$ |
| 20 N* till. + 20 N + ear em. | 21.6$^{a}$ | 4.0$^{ab}$ | 25.6$^{a}$ | — | — | — | — | — | — | — |
| 20 N till. + 20 N* + ear em. | 15.4$^{ab}$ | 2.6$^{bc}$ | 18.0$^{ab}$ | — | — | — | — | — | — | — |
| 1989 | | | | | | | | | | |
| 40 N* spring | 33.5$^{a}$ | 15.9$^{a}$ | 49.4$^{a}$ | 30.5$^{a}$ | 2.4$^{a}$ | 5.1$^{a}$ | 37.9$^{a}$ | 87.4$^{a}$ | 10.1$^{a}$ | 2.5$^{a}$ |
| 40 N* tillering | 27.5$^{ab}$ | 12.7$^{b}$ | 40.2$^{ab}$ | 42.3$^{a}$ | 4.7$^{a}$ | 1.6$^{a}$ | 48.6$^{a}$ | 88.8$^{a}$ | 6.6$^{a}$ | 4.6$^{a}$ |
| 40 N* ear emergence | 31.0$^{a}$ | 12.5$^{b}$ | 43.4$^{a}$ | 35.0$^{a}$ | 9.8$^{a}$ | 0.2$^{a}$ | 44.9$^{a}$ | 88.4$^{a}$ | 3.5$^{a}$ | 8.1$^{a}$ |
| 40 N* urea, tillering | 11.4$^{c}$ | 4.4$^{d}$ | 15.8$^{c}$ | 39.6$^{a}$ | 12.0$^{a}$ | 4.0$^{a}$ | 55.7$^{a}$ | 71.5$^{a}$ | 10.6$^{a}$ | 17.8$^{a}$ |
| 40 N* urea, ear emergence | 21.3$^{b}$ | 7.4$^{c}$ | 28.7$^{b}$ | 42.5$^{a}$ | 12.2$^{a}$ | 6.3$^{a}$ | 61.0$^{a}$ | 89.8$^{a}$ | 9.2$^{a}$ | 1.1$^{a}$ |
| 1990 | | | | | | | | | | |
| 40 N* spring | 36.8$^{ab}$ | 12.8$^{a}$ | 49.7$^{abc}$ | 39.8$^{ab}$ | 1.1$^{a}$ | 0.7$^{a}$ | 41.6$^{ab}$ | 91.3$^{ab}$ | — | 8.7$^{ab}$ |
| 40 N* tillering | 43.3$^{a}$ | 11.5$^{a}$ | 54.8$^{ab}$ | 35.6$^{ab}$ | −0.1$^{a}$ | 0.2$^{a}$ | 35.7$^{ab}$ | 90.4$^{ab}$ | — | 9.6$^{ab}$ |
| 40 N* ear emergence | 47.2$^{a}$ | 12.9$^{a}$ | 60.1$^{a}$ | 31.1$^{b}$ | 2.8$^{a}$ | −0.1$^{a}$ | 33.8$^{ab}$ | 93.9$^{a}$ | — | 6.1$^{b}$ |
| 40 N* urea, tillering | 27.5$^{b}$ | 9.6$^{a}$ | 37.1$^{c}$ | 50.2$^{a}$ | 1.4$^{a}$ | 1.2$^{a}$ | 52.7$^{a}$ | 89.9$^{ab}$ | — | 10.1$^{ab}$ |
| 40 N* urea, ear emergence | 31.1$^{b}$ | 10.2$^{a}$ | 41.3$^{bc}$ | 28.8$^{b}$ | −1.0$^{a}$ | −1.1$^{a}$ | 26.7$^{b}$ | 68.0$^{b}$ | — | 32.0$^{a}$ |

In 1987, fertilizer application at ear emergency resulted in the highest recovery. The recovery of nitrogen applied at sowing was only about half that of the nitrogen applied at ear emergence. The difference was statistically significant. Splitting the application into two 20 + 20 kg/ha portions at tillering and at ear emergence resulted in a statistically significantly lower recovery compared to a single dressing at the corresponding growth stage. The total recoveries of fertilizer nitrogen in the crops correlated with the recoveries in the grain and straw.

In 1987, about 68 % (27 kg) of the applied 40 kg/ha of nitrogen was recovered in the plants and in a 90 cm layer of soil from the spring application of nitrogen. The corresponding recovery for the application at the tillering stage was 91 % (36 kg) and for the application at ear emergence 98 %. The loss of the labelled nitrogen being 2—32 %. Not even the great difference between the earliest and latest application was statistically significant (MSD 36.8 %, P = 0.10).

In 1987, the differences between the times of application in the total recovery of nitrogen can be explained mainly by the differences in the recoveries in the crop. In the 0—90 cm soil layer the differences were about 8 percentage units. The results of the recoveries in the soil are, however, uncertain, because the enrichment of $^{15}N$ in the fertilizer was only 5 %, which was not enough to show so small amounts of labelled fertilizer in the soil accurately.

In 1988, the recovery of $^{15}N$ in the above ground parts of the crops was statistically significantly lower than in 1987. The effect of time of application on the recovery was almost opposite to 1987. The recovery from the application of nitrogen at ear emergence was statistically significantly lower than from the application at sowing. The recovery from the application at tillering ranged, as also in the previous year, between the recoveries from the other two applications, although it did not differ statistically significantly from the other applications. An opposite result to the previous year, although not statistically significant, was also the higher recovery from the splitted two 20 + 20 kg/ha portions compared to the single application at the corresponding growth stage.

In 1988, about 96 % of the 40 kg/ha nitrogen applied at sowing was recovered in the crops and in the 90 cm soil layer whereas the recovery from the application at ear emergence was only about 64 %. This difference was statistically significant. The greatest proportion of the fertilizer nitrogen was recovered in the topsoil; and the differences between the treatments were greatest, 18.7 %, although not statistically significant (P = 7.2, MSD = 20.1 %). The amount of fertilizer nitrogen unaccounted for was surprisingly high, 36 % (14 kg/ha) from the application at ear emergence. The amounts of residual labelled nitrogen in the soil were higher in 1988 than in 1987, which gave a higher difference between the background labelling of the soil and the labelling on the $^{15}N$ fertilized plots. So the 1988 results are more reliable than the 1987 results.

In 1989 and 1990, the differences of the recoveries of fertilizer nitrogen in the crop between the treatments in question were smaller and statistically insignificant. The higher result for the spring application in 1989 was probably a consequence of an experimental error caused by braking the crust of the soil surface by the fertilizer application at sowing, which resulted in better growth of the crops in these plots.

In 1989, the recovery of labelled nitrogen in the crop and in the 0—90 cm soil profile was 87—89 % for the treatments in question. The weeds (red dead-nettle, *Lamium purpureum* L.) contained 4—11 % of the labelled nitrogen applied. So the amount of unaccounted for nitrogen was 3—8 % of that applied. None of these differences were statistically significant.

In 1990, the recovery of labelled nitrogen in the plant-soil system was high (91—94 %) and

the differences between the treatments were statistically insignificant, when comparing spring applications and top dressings. The results concerning the recoveries of fertilizer nitrogen in the soil are more accurate in 1990, because the enrichment of $^{15}N$ in the fertilizer was higher, 10 atom %, than in previous years.

In 1989, the roots were separated from the top soil samples. The recovery of labelled nitrogen in the roots was 3.0—5.5 % and there were no statistically significant differences between the treatments. So the recoveries in the roots were added up with those of the top soil.

The recoveries of nitrogen from urea sprayings were lower than from the application as nitrate nitrogen on the soil surface at corresponding growth stages. In 1990, the recoveries of urea originating labelled nitrogen in the soil were not different from the other treatments, but they were different from each other. The recovery of urea sprayed at tillering was highest and that from ear emergence was lowest. The recoveries of nitrogen in the soil originating from urea are again uncertain because of low enrichment of the fertilizer nitrogen.

In 1989, the total recoveries from urea spraying at tillering were lower, but not statistically significantly. In 1990, the recovery from urea spraying at ear emergence was statistically significantly lower than the recovery of nitrate applied by top dressing at the same growth stage. The losses were correspondingly higher from these treatments.

The time of application or the form of nitrogen applied did not affect the amount of nitrogen taken up by the crops from other sources than the $^{15}N$-labelled nitrogen statistically significantly in any of the years (Table 19).

In 1987, the plants had taken up from the spring application about 74 % of their total uptake of nitrogen at anthesis (Table 20). From the top dressings the corresponding amount was 40—50 % and there was no statistically significant difference between the top dressings. In 1988, the plants had taken up from the spring application about 87 % of their total amount of labelled nitrogen at anthesis, 45—50 % from

Table 19. The total uptake of nitrogen as well as uptake of labelled and unlabelled nitrogen by the crops in the field experiment with $^{15}N$ labelled nitrogen (= *). The results within the same year and same column followed by the same letter do not differ statistically significantly according to Tukey's test (P = 0.05).

| Nitrogen fertilizer application | Nitrogen uptake, kg/ha | | | | | |
|---|---|---|---|---|---|---|
| | Labelled nitrogen | Unlabelled nitrogen | Total uptake | Labelled nitrogen | Unlabelled nitrogen | Total uptake |
| | 1987 | | | 1988 | | |
| Unfertilized | — | — | 33.9$^{d}$ | — | — | 31.7$^{b}$ |
| 100 kg/ha spring | — | — | 72.0$^{c}$ | — | — | 76.5$^{a}$ |
| 100 » +40 N* spring | 12.9$^{b}$ | 72.5$^{a}$ | 85.4$^{bc}$ | 10.1$^{a}$ | 59.4$^{a}$ | 69.4$^{a}$ |
| 100 » +40 N* tillering | 25.2$^{a}$ | 74.3$^{a}$ | 99.4$^{ab}$ | 8.5$^{ab}$ | 65.8$^{a}$ | 74.2$^{a}$ |
| 100 » +40 N* ear emergence | 27.5$^{a}$ | 78.7$^{a}$ | 106.1$^{a}$ | 5.8$^{b}$ | 61.6$^{a}$ | 67.4$^{a}$ |
| 100 » +20 N* till. +20 N ear em. | — | — | 103.4$^{a}$ | — | — | 73.2$^{a}$ |
| 100 » +20 N till. +20 N* ear em. | — | — | 98.3$^{ab}$ | — | — | 73.8$^{a}$ |
| | 1989 | | | 1990 | | |
| Unfertilized | — | — | 44.2$^{c}$ | — | — | 56.5$^{b}$ |
| 100 kg/ha spring | — | — | 96.7$^{ab}$ | — | — | 117.8$^{a}$ |
| 100 » +40 N* spring | 19.8$^{a}$ | 100.5$^{a}$ | 120.3$^{a}$ | 19.9$^{abc}$ | 97.2$^{a}$ | 117.1$^{a}$ |
| 100 » +40 N* tillering | 16.1$^{ab}$ | 78.4$^{a}$ | 94.4$^{b}$ | 21.9$^{ab}$ | 98.2$^{a}$ | 120.1$^{a}$ |
| 100 » +40 N* ear emergence | 17.4$^{a}$ | 84.1$^{a}$ | 101.4$^{ab}$ | 24.0$^{a}$ | 97.9$^{a}$ | 121.9$^{a}$ |
| 100 » +40 N* urea, tillering | 6.3$^{c}$ | 87.3$^{a}$ | 93.6$^{b}$ | 14.9$^{c}$ | 109.3$^{a}$ | 124.1$^{a}$ |
| 100 » +40 N* urea, ear emergence | 11.5$^{b}$ | 82.4$^{a}$ | 93.9$^{b}$ | 16.5$^{bc}$ | 109.7$^{a}$ | 126.3$^{a}$ |

the application at tillering and 6—7 % from the application at ear emergence. The figures for 1989 were 81 %, 15 % and 1 % and for 1990 62 %, 43 % and 21 %, respectively.

At anthesis, the recovery of nitrogen from urea spraying was 25 % and 27 % of the total uptake for the application at tillering in 1989 and 1990, respectively, and 59 % and 30 % for the applications at ear emergence, respectively.

### 5.3.3. Extractable inorganic nitrogen in soil at harvest

The amount of inorganic nitrogen extracted by 2 M KCl in the 0—90 cm soil layer at harvest was on the fertilized plots 25—30 kg/ha in 1987, 113—260 kg/ha in 1988, 48—80 kg/ha in 1989 and 57—83 kg/ha in 1990 (Table 21). The amount of inorganic nitrogen on the unfertilized plots was about the same as that of

Table 20. The effect of nitrogen fertilizer and time of application of nitrogen fertilizer as top dressing to spring wheat on the dry matter yield, uptake of nitrogen and recovery of $^{15}N$-labelled fertilizer nitrogen at anthesis in 1987—1990. The results within the same year and the same column followed by the same letter do not differ statistically significantly according to the Tukey's test (P = 0.05).

| Fertilizer application | Yield kg/ha DM | Nitrogen yield kg/ha | Recovery of $^{15}N$-labelled nitrogen | | |
|---|---|---|---|---|---|
| | | | kg/ha | % of applied | % of total uptake |
| 1987 | | | | | |
| Unfertilizerd | 2380$^{b}$ | 26.3$^{c}$ | — | — | — |
| 100 kg/ha N spring | 4390$^{a}$ | 56.3$^{b}$ | — | — | — |
| 100 » + 40 N* spring | 4670$^{a}$ | 66.6$^{ab}$ | 9.6$^{a}$ | 24.0$^{a}$ | 74.1$^{a}$ |
| 100 » + 40 N* tillering | 4630$^{a}$ | 72.9$^{a}$ | 11.1$^{a}$ | 27.8$^{a}$ | 44.2$^{b}$ |
| 100 » + 40 N* ear emergence | 4320$^{a}$ | 71.0$^{a}$ | 11.0$^{a}$ | 27.6$^{a}$ | 40.2$^{b}$ |
| 100 » + 20 N* till. + 20 N ear em. | 4490$^{a}$ | 68.8$^{ab}$ | 4.4$^{b}$ | 22.2$^{a}$ | 43.0$^{b}$ |
| 100 » + 20 N till. + 20 N* ear em. | 4600$^{a}$ | 77.6$^{a}$ | 5.7$^{b}$ | 28.7$^{a}$ | 49.0$^{b}$ |
| 1988 | | | | | |
| Unfertilized | 1230$^{b}$ | 15.3$^{b}$ | — | — | — |
| 100 kg/ha N spring | 3060$^{a}$ | 58.0$^{a}$ | — | — | — |
| 100 » + 40 N* spring | 2750$^{a}$ | 56.4$^{a}$ | 8.4$^{a}$ | 20.9$^{a}$ | 86.8$^{a}$ |
| 100 » + 40 N* tillering | 2650$^{a}$ | 51.4$^{a}$ | 3.7$^{b}$ | 9.3$^{b}$ | 50.3$^{b}$ |
| 100 » + 40 N* ear emergence | 2700$^{a}$ | 60.0$^{a}$ | 0.4$^{c}$ | 0.9$^{c}$ | 7.0$^{c}$ |
| 100 » + 20 N* till. + 20 N ear em. | 2560$^{a}$ | 53.2$^{a}$ | 2.1$^{bc}$ | 10.4$^{b}$ | 44.3$^{b}$ |
| 100 » + 20 N till. + 20 N* ear em. | 2900$^{a}$ | 58.0$^{a}$ | 0.2$^{c}$ | 0.5$^{c}$ | 6.4$^{c}$ |
| 1989 | | | | | |
| Unfertilized | 1300$^{b}$ | 18.0$^{b}$ | — | — | — |
| 100 kg/ha N spring | 2080$^{ab}$ | 42.8$^{ab}$ | — | — | — |
| 100 » + 40 N* spring | 3500$^{a}$ | 84.7$^{a}$ | 15.9$^{a}$ | 39.8$^{a}$ | 81.3$^{a}$ |
| 100 » + 40 N* tillering | 2530$^{ab}$ | 55.9$^{ab}$ | 2.3$^{bc}$ | 5.9$^{bc}$ | 14.7$^{c}$ |
| 100 » + 40 N* ear emergence | 2380$^{ab}$ | 54.6$^{ab}$ | 0.3$^{c}$ | 0.7$^{c}$ | 1.4$^{c}$ |
| 100 » + 40 N* urea, tillering | 2070$^{ab}$ | 43.6$^{ab}$ | 1.6$^{bc}$ | 4.1$^{bc}$ | 27.1$^{bc}$ |
| 100 » + 40 N* urea, ear emergence | 2010$^{ab}$ | 48.5$^{ab}$ | 6.8$^{b}$ | 17.0$^{b}$ | 59.2$^{ab}$ |
| 1990 | | | | | |
| Unfertilized | 2180$^{b}$ | 32.5$^{b}$ | — | — | — |
| 100 kg/ha N spring | 3140$^{a}$ | 65.3$^{a}$ | — | — | — |
| 100 » + 40 N. spring | 2930$^{ab}$ | 67.2$^{a}$ | 12.2$^{a}$ | 30.6$^{a}$ | 61.8$^{a}$ |
| 100 » + 40 N* tillering | 3310$^{a}$ | 72.0$^{a}$ | 9.4$^{b}$ | 23.5$^{b}$ | 43.2$^{b}$ |
| 100 » + 40 N* ear emergence | 3160$^{a}$ | 68.2$^{a}$ | 5.0$^{c}$ | 12.5$^{c}$ | 20.8$^{c}$ |
| 100 » + 40 N* urea, tillering | 3020$^{ab}$ | 68.2$^{a}$ | 3.7$^{c}$ | 9.3$^{c}$ | 25.4$^{c}$ |
| 100 » + 40 N* urea, ear emergence | 3180$^{a}$ | 66.8$^{a}$ | 4.8$^{c}$ | 12.1$^{c}$ | 29.4$^{c}$ |

Table 21. The effect of nitrogen fertilizer and time of application of nitrogen fertilizer as top dressing to spring wheat on the amounts of inorganic nitrogen, nitrate nitrogen and ammonium nitrogen in the soil at harvest in 1987—1990. * = $^{15}$N-labelled fertilizer. The results within the same year and the same column followed by the same letter do not differ statistically significantly according to Tukey's (P = 0.05). MSD = minimum significant difference.

| Fertilizer application | Inorganic N, kg/ha | | | | Nitrate N, kg/ha | | | | Ammonium N, kg/ha | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0—25 cm | 25—60 cm | 60—90 cm | total | 0—25 cm | 25—60 cm | 60—90 cm | total | 0—25 cm | 25—60 cm | 60—90 cm | total |
| 1987 | | | | | | | | | | | | |
| Unfertilized | 11.8$^{b}$ | 11.9$^{a}$ | 4.5$^{a}$ | 28.2$^{ab}$ | 1.2$^{b}$ | 3.0$^{a}$ | 0.3$^{a}$ | 4.6$^{a}$ | 10.5$^{ab}$ | 8.8$^{a}$ | 4.2$^{a}$ | 23.6$^{ab}$ |
| 100 N, spring | 12.4$^{b}$ | 8.1$^{ab}$ | 4.0$^{ab}$ | 24.5$^{b}$ | 2.4$^{a}$ | 1.7$^{b}$ | 0.2$^{b}$ | 4.2$^{a}$ | 10.0$^{b}$ | 6.4$^{a}$ | 3.8$^{ab}$ | 20.3$^{b}$ |
| 100 » + 40 N* spring | 12.3$^{b}$ | 8.7$^{ab}$ | 3.5$^{b}$ | 24.5$^{b}$ | 2.6$^{a}$ | 1.7$^{b}$ | 0.2$^{b}$ | 4.4$^{a}$ | 9.7$^{b}$ | 7.0$^{a}$ | 3.3$^{b}$ | 20.0$^{b}$ |
| 100 » + 40 N* tillering | 12.8$^{b}$ | 8.0$^{b}$ | 3.8$^{b}$ | 24.6$^{b}$ | 2.7$^{a}$ | 1.9$^{b}$ | 0.2$^{ab}$ | 4.8$^{a}$ | 10.1$^{ab}$ | 6.1$^{a}$ | 3.6$^{b}$ | 19.8$^{b}$ |
| 100 » + 40 N* ear emergence | 15.2$^{a}$ | 11.0$^{ab}$ | 3.9$^{b}$ | 30.1$^{a}$ | 2.9$^{ab}$ | 2.3$^{b}$ | 0.3$^{ab}$ | 5.5$^{a}$ | 12.3$^{a}$ | 8.7$^{a}$ | 3.6$^{b}$ | 24.6$^{a}$ |
| MSD | 2.3 | 3.9 | 0.6 | 5.2 | 0.9 | 1.0 | 0.1 | 1.6 | 2.2 | 3.0 | 0.5 | 4.2 |
| 1988 | | | | | | | | | | | | |
| Unfertilized | 14.2$^{c}$ | 7.2$^{b}$ | 4.5$^{a}$ | 25.9$^{b}$ | 5.3$^{d}$ | 4.6$^{b}$ | 3.1$^{a}$ | 13.0$^{b}$ | 8.8$^{b}$ | 2.6$^{a}$ | 1.4$^{a}$ | 12.9$^{b}$ |
| 100 N, spring | 41.1$^{bc}$ | 52.7$^{ab}$ | 34.3$^{a}$ | 128.0$^{ab}$ | 27.9$^{c}$ | 35.2$^{ab}$ | 23.1$^{a}$ | 86.2$^{b}$ | 13.2$^{b}$ | 17.5$^{a}$ | 11.1$^{a}$ | 41.8$^{ab}$ |
| 100 » + 40 N* spring | 114.8$^{a}$ | 118.7$^{a}$ | 26.7$^{a}$ | 260.2$^{a}$ | 75.9$^{a}$ | 74.4$^{a}$ | 20.1$^{a}$ | 170.4$^{a}$ | 38.9$^{a}$ | 44.3$^{a}$ | 6.6$^{a}$ | 89.8$^{a}$ |
| 100 » + 40 N* tillering | 73.2$^{b}$ | 27.4$^{ab}$ | 12.2$^{a}$ | 112.8$^{b}$ | 55.8$^{b}$ | 21.9$^{ab}$ | 8.8$^{a}$ | 86.4$^{b}$ | 17.4$^{b}$ | 5.5$^{a}$ | 3.4$^{a}$ | 26.4$^{b}$ |
| 100 » + 40 N* ear emergence | 73.5$^{b}$ | 24.8$^{ab}$ | 14.7$^{a}$ | 113.0$^{b}$ | 52.8$^{b}$ | 20.6$^{ab}$ | 9.5$^{a}$ | 82.9$^{b}$ | 20.7$^{b}$ | 4.2$^{a}$ | 5.1$^{a}$ | 30.1$^{ab}$ |
| MSD | 33.0 | 101.8 | 34.7 | 138.8 | 19.6 | 59.1 | 23.8 | 80.5 | 16.6 | 43.1 | 11.1 | 60.4 |
| 1989 | | | | | | | | | | | | |
| Unfertilized | 17.8$^{b}$ | 12.7$^{c}$ | 6.0$^{a}$ | 36.4$^{b}$ | 9.0$^{b}$ | 10.9$^{c}$ | 4.3$^{a}$ | 24.2$^{c}$ | 8.8$^{a}$ | 1.7$^{a}$ | 1.6$^{ab}$ | 12.2$^{a}$ |
| 100 N, spring | 26.6$^{b}$ | 16.9$^{bc}$ | 7.0$^{a}$ | 50.4$^{b}$ | 20.8$^{b}$ | 14.9$^{abc}$ | 5.6$^{a}$ | 41.3$^{bc}$ | 5.9$^{a}$ | 1.9$^{a}$ | 1.4$^{b}$ | 9.2$^{a}$ |
| 100 » + 40 N* spring | 24.8$^{b}$ | 16.8$^{bc}$ | 6.7$^{a}$ | 48.3$^{b}$ | 18.3$^{b}$ | 14.3$^{bc}$ | 4.9$^{a}$ | 37.5$^{c}$ | 6.5$^{a}$ | 2.4$^{a}$ | 1.8$^{ab}$ | 10.8$^{a}$ |
| 100 » + 40 N* tillering | 47.6$^{a}$ | 19.7$^{ab}$ | 8.1$^{a}$ | 75.4$^{a}$ | 41.4$^{a}$ | 17.6$^{ab}$ | 6.1$^{a}$ | 65.1$^{a}$ | 6.2$^{a}$ | 2.1$^{a}$ | 2.0$^{a}$ | 10.3$^{a}$ |
| 100 » + 40 N* ear emergence | 43.3$^{a}$ | 18.6$^{abc}$ | 8.7$^{a}$ | 70.6$^{a}$ | 36.4$^{a}$ | 16.7$^{abc}$ | 6.9$^{a}$ | 59.9$^{a}$ | 6.9$^{a}$ | 1.9$^{a}$ | 1.8$^{ab}$ | 10.6$^{a}$ |
| 100 » + 40 N*urea, tillering | 40.0$^{a}$ | 20.3$^{ab}$ | 8.3$^{a}$ | 68.7$^{a}$ | 33.7$^{a}$ | 18.0$^{ab}$ | 6.4$^{a}$ | 58.1$^{ab}$ | 6.3$^{a}$ | 2.3$^{a}$ | 1.9$^{ab}$ | 10.5$^{a}$ |
| 100 » + 40 N*urea, ear emergence | 47.6$^{a}$ | 23.2$^{a}$ | 9.0$^{a}$ | 79.8$^{a}$ | 41.1$^{a}$ | 20.7$^{a}$ | 7.2$^{a}$ | 69.1$^{a}$ | 6.4$^{a}$ | 2.6$^{a}$ | 1.7$^{ab}$ | 10.7$^{a}$ |
| MSD | 12.9 | 6.3 | 3.6 | 18.1 | 12.6 | 5.9 | 3.4 | 17.7 | 3.3 | 0.9 | 0.5 | 3.7 |
| 1990 | | | | | | | | | | | | |
| Unfertilized | — | — | — | — | — | — | — | — | — | — | — | — |
| 100 N, spring | 26.5$^{d}$ | 12.6$^{a}$ | 8.7$^{a}$ | 47.8$^{d}$ | 19.6$^{d}$ | 9.9$^{a}$ | 7.4$^{a}$ | 36.9$^{d}$ | 7.0$^{ab}$ | 2.6$^{a}$ | 1.3$^{a}$ | 10.9$^{a}$ |
| 100 » + 40 N* spring | 62.3$^{a}$ | 13.2$^{a}$ | 7.5$^{ab}$ | 83.0$^{a}$ | 55.5$^{a}$ | 10.4$^{a}$ | 6.1$^{ab}$ | 72.0$^{a}$ | 6.8$^{ab}$ | 2.8$^{a}$ | 1.4$^{a}$ | 11.0$^{a}$ |
| 100 » + 40 N* tillering | 53.1$^{ab}$ | 13.0$^{a}$ | 7.7$^{ab}$ | 73.8$^{ab}$ | 45.7$^{ab}$ | 10.2$^{a}$ | 6.5$^{ab}$ | 62.4$^{ab}$ | 7.5$^{ab}$ | 2.8$^{a}$ | 1.2$^{a}$ | 11.5$^{a}$ |
| 100 » + 40 N* ear emergence | 47.5$^{bc}$ | 11.6$^{a}$ | 7.4$^{ab}$ | 66.4$^{bc}$ | 39.6$^{bc}$ | 9.2$^{a}$ | 5.9$^{ab}$ | 54.8$^{bc}$ | 7.8$^{ab}$ | 2.4$^{a}$ | 1.5$^{a}$ | 11.7$^{a}$ |
| 100 » + 40 N*urea, tillering | 37.6$^{cd}$ | 12.5$^{a}$ | 6.6$^{b}$ | 56.7$^{cd}$ | 31.3$^{c}$ | 9.9$^{a}$ | 5.4$^{b}$ | 46.5$^{cd}$ | 6.3$^{b}$ | 2.6$^{a}$ | 1.2$^{a}$ | 10.1$^{a}$ |
| 100 » + 40 N*urea, ear emergence | 42.6$^{bc}$ | 11.4$^{a}$ | 6.0$^{b}$ | 60.0$^{c}$ | 33.5$^{c}$ | 9.1$^{a}$ | 5.0$^{b}$ | 47.6$^{cd}$ | 9.1$^{a}$ | 2.3$^{a}$ | 1.1$^{a}$ | 12.5$^{a}$ |
| MSD | 11.1 | 2.7 | 1.7 | 11.7 | 11.5 | 2.4 | 1.7 | 12.0 | 2.5 | 0.7 | 0.4 | 2.6 |

the fertilized plots in 1987, but was lower than on the fertilized plots in 1988—1990. The proportion of inorganic nitrogen in the top 25 cm soil layer of the total inorganic nitrogen in the 0—90 cm layer of the fertilized plots was about 50 % in 1987, 50—65 % in 1988—89 and 65—75 % in 1990.

In the ample moisture conditions of 1987 the amount of residual inorganic nitrogen was mostly ammonium nitrogen, and nitrate covered 18 % of inorganic nitrogen (Table 21). In 1989 and 1990, the amount of ammonium nitrogen was quite stable, 10—12 kg/ha in the whole 0—90 cm soil layer, and the inorganic nitrogen consisted 83 % on average of nitrate nitrogen in both years. In 1988, when the inorganic nitrogen contents were the highest, also the ammonium nitrogen contents were higher and nitrate covered 69 % on average of the inorganic nitrogen in the whole soil layer.

In 1987, the latest application at ear emergence resulted in a statistically significant increase of residual inorganic nitrogen in the 0—90 cm soil profile of about 5 kg/ha and a statistically significant increase of inorganic nitrogen in the top 25 cm layer of about 2.5 kg/ha.

In 1988, the applications at tillering resulted in about double the amount of residual inorganic nitrogen in the profile compared to the other treatments. This result is difficult to explain and can be suspected to be due to some kind of experimental error. The spatial variability and the MSD values were high in 1988. So, perhaps the sampling was not made representatively. Twenty subsamples were taken from the topsoil, but in the dry conditions with large amounts of unused fertilizer nitrogen in bands, this may not be the right way to get representative samples. The system was improved for 1989 and 1990. The amounts of inorganic nitrogen as a whole were high in 1988. The fact that the samples were stored frozen until analysis of inorganic nitrogen in spring 1991 did not obviously affect the results remarkably.

In 1989, all the top dressings resulted in statistically significantly higher amounts of inorganic nitrogen in the soil compared to the spring application or the lower amounts of fertilizer or the unfertilized plots. In 1990, both spring application and top dressing at tillering tended to leave more inorganic nitrogen in the soil than the top dressing at ear emergence or the urea sprayings.

The proportion of labelled inorganic nitrogen of the total inorganic nitrogen in the 0—90 cm profile was low in 1987 (1.5—2.6 %) and highest in 1988 (11.4—19.9 %). In 1989 it was 6.8—13.8 % and in 1990 9.4—12.9 % comparing the treatments, except for urea sprayings (Table 22).

The top dressings of nitrate nitrogen resulted in a statistically significantly higher proportion of labelled inorganic nitrogen in all the years, except 1990, when the top dressings retained relatively less inorganic nitrogen compared to the spring applications. Urea sprayings resulted in a smaller proportion of labelled inorganic nitrogen in the soil than the nitrate top dressings.

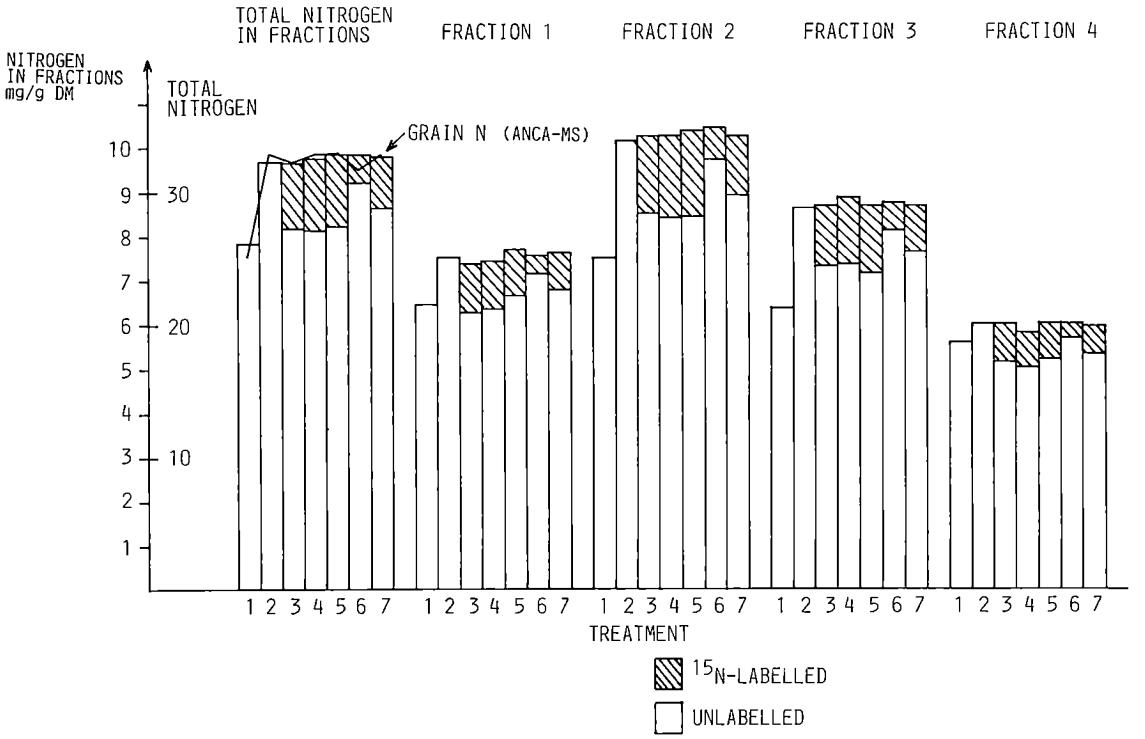
In 1988 and 1989, the proportion of labelled inorganic nitrogen of the total inorganic nitrogen was about the same in the 0—25 cm and 25—60 cm soil layers and considerably less, about 1/3—1/4 in 1987 and 1990. In the 60—90 cm soil layer the proportion in question was generally lower than in the other two layers, except in 1987, when the proportion was about the same in the 25—60 cm and 60—90 cm layers. The proportion of labelled inorganic nitrogen in the 0—25 cm layer of the amount of labelled inorganic nitrogen in the whole 0—90 cm profile was 67—86 % in 1987, 68—79 % in 1988, 54—71 % in 1989 and 81—94 % in 1990.

The recovery of labelled nitrogen as inorganic nitrogen in the 0—90 cm profile of the total amount, 40 kg/ha, applied was 0.9—

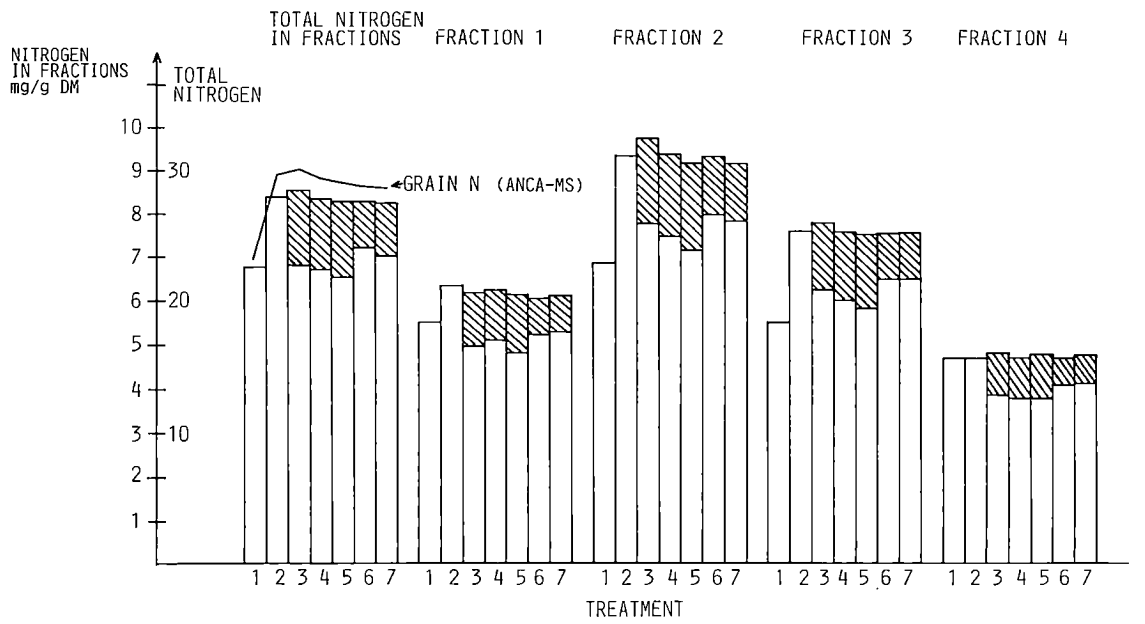
Table 22. The effect of nitrogen fertilizer and time of application of nitrogen fertilizer as top dressing to spring wheat on the recovery of $^{15}N$-labelled fertilizer (= *) as the residual total nitrogen and inorganic nitrogen in the soil at harvest in 1987—1990. The results within the same year and the same column followed by the same letter do not differ statistically significantly according to Tukey's test (P = 0.05). MSD = minimum significant difference.

| Fertilizer application | Total labelled N in soil at harvest kg/ha | | | | Labelled inorganic N in soil at harvest kg/ha | | | | Labelled inorganic N in soil at harvest as % of total inorganic N | | | | Labelled inorganic N in soil at harvest as % of labelled N applied | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0—25 cm | 25—60 cm | 60—90 cm | total | 0—25 cm | 25—60 cm | 60—90 cm | total | 0—25 cm | 25—60 cm | 60—90 cm | total | 0—25 cm | 25—60 cm | 60—90 cm | total |
| 1987 | | | | | | | | | | | | | | | | |
| 100 + 40 N* spring | 9.5[a] | 4.6[a] | 0.0[a] | 14.1[a] | 0.3[b] | 0.1[a] | 0.0[a] | 0.4[b] | 2.1[b] | 0.7[a] | 1.4[a] | 1.5[b] | 0.6[b] | 0.1[a] | 0.1[a] | 0.9[b] |
| 100 + 40 N* tillering | 10.4[a] | 0.4[a] | 0.2[a] | 11.0[a] | 0.5[a] | 0.0[a] | 0.0[a] | 0.6[ab] | 3.6[a] | 0.6[a] | 1.0[a] | 2.2[a] | 1.2[a] | 0.1[a] | 0.1[a] | 1.4[ab] |
| 100 + 40 N* ear emergenge | 10.7[a] | 0.6[a] | 0.3[a] | 11.6[a] | 0.6[a] | 0.1[a] | 0.0[a] | 0.8[a] | 4.1[a] | 1.1[a] | 0.8[a] | 2.6[a] | 1.6[a] | 0.3[a] | 0.1[a] | 1.9[a] |
| MSD | 14.3 | 5.2 | 0.7 | 14.2 | 0.2 | 0.1 | 0.0 | 0.2 | 1.3 | 1.8 | 1.0 | 0.7 | 0.5 | 0.3 | 0.1 | 0.6 |
| 1988 | | | | | | | | | | | | | | | | |
| 100 + 40 N* spring | 21.4[a] | 5.4[a] | 1.5[a] | 28.2[a] | 13.0[b] | 4.5[a] | 1.7[a] | 19.2[a] | 13.0[c] | 10.4[a] | 10.9[a] | 11.4[b] | 32.6[b] | 11.2[a] | 4.2[a] | 47.9[a] |
| 100 + 40 N* tillering | 18.9[a] | 3.8[a] | 0.6[a] | 23.3[ab] | 16.9[a] | 3.8[a] | 0.8[b] | 21.6[a] | 23.8[a] | 16.8[a] | 11.1[a] | 19.9[a] | 42.3[a] | 9.5[a] | 2.1[b] | 53.9[a] |
| 100 + 40 N* ear emergence | 13.9[a] | 5.2[a] | 0.6[a] | 19.7[b] | 13.4[b] | 4.1[a] | 1.3[ab] | 18.8[a] | 18.5[b] | 17.0[a] | 11.7[a] | 17.1[a] | 33.6[b] | 10.2[a] | 3.3[ab] | 47.1[a] |
| MSD | 8.1 | 4.2 | 1.4 | 6.6 | 2.7 | 2.5 | 0.8 | 3.7 | 4.1 | 8.0 | 4.4 | 3.3 | 6.8 | 6.2 | 1.9 | 9.4 |
| 1989 | | | | | | | | | | | | | | | | |
| 100 + 40 N* spring | 12.2[a] | 1.0[a] | 2.0[a] | 15.2[a] | 1.9[d] | 1.2[c] | 0.2[c] | 3.3[c] | 7.5[bc] | 7.8[bc] | 2.8[c] | 6.8[b] | 4.7[d] | 3.1[c] | 0.5[c] | 8.2[c] |
| 100 + 40 N* tillering | 16.9[a] | 1.9[a] | 0.7[a] | 19.4[a] | 7.0[a] | 2.8[a] | 0.7[ab] | 10.6[a] | 14.5[a] | 14.4[a] | 8.8[ab] | 13.8[a] | 17.6[a] | 7.0[a] | 1.8[ab] | 26.4[a] |
| 100 + 40 N* ear emergence. | 14.0[a] | 3.9[a] | 0.1[a] | 17.8[a] | 6.6[ab] | 2.3[ab] | 0.4[abc] | 9.2[ab] | 15.0[a] | 12.6[ab] | 5.3[abc] | 13.1[a] | 16.4[ab] | 5.6[ab] | 1.0[abc] | 23.1[ab] |
| 100 + 40 N*ur tillering | 15.8[a] | 4.8[a] | 1.6[a] | 22.3[a] | 2.2[cd] | 1.1[c] | 0.8[a] | 4.2[c] | 5.5[c] | 5.6[c] | 9.7[a] | 6.2[b] | 5.6[cd] | 2.7[c] | 2.0[a] | 10.4[c] |
| 100 + 40 N*ur ear emerg. | 17.0[a] | 4.9[a] | 2.5[a] | 24.4[a] | 4.4[bc] | 1.5[bc] | 0.3[bc] | 6.2[bc] | 9.2[b] | 7.1[bc] | 4.6[bc] | 8.1[b] | 10.9[bc] | 3.7[bc] | 0.9[bc] | 15.5[bc] |
| MSD | 9.0 | 5.1 | 5.4 | 12.7 | 2.4 | 1.0 | 0.4 | 3.4 | 2.4 | 6.3 | 4.5 | 3.1 | 5.9 | 2.5 | 1.0 | 8.4 |
| 1990 | | | | | | | | | | | | | | | | |
| 100 + 40 N* spring | 17.6[ab] | 0.5[a] | 0.3[a] | 18.4[ab] | 10.1[a] | 0.6[ab] | 0.1[ab] | 10.8[a] | 16.2[a] | 4.6[ab] | 0.9[a] | 12.9[a] | 25.3[a] | 1.5[ab] | 0.2[ab] | 27.0[a] |
| 100 + 40 N* tillering | 14.2[ab] | −0.1[a] | 0.1[a] | 14.3[ab] | 7.6[b] | 0.4[bc] | 0.1[ab] | 8.0[b] | 14.0[a] | 3.1[b] | 0.8[a] | 10.7[b] | 18.9[b] | 1.0[bc] | 0.2[ab] | 20.1[b] |
| 100 + 40 N* ear emergence | 12.5[b] | 1.1[a] | 0.0[a] | 13.5[ab] | 5.5[b] | 0.7[a] | 0.1[a] | 6.4[b] | 11.4[b] | 6.0[a] | 1.7[a] | 9.4[b] | 13.9[b] | 1.7[a] | 0.3[a] | 15.9[b] |
| 100 + 40 N*ur tillering | 20.1[a] | 0.6[a] | 0.5[a] | 21.1[a] | 1.9[c] | 0.3[c] | 0.1[ab] | 2.3[c] | 5.0[c] | 2.8[b] | 1.9[a] | 4.1[c] | 4.7[c] | 0.8[c] | 0.2[ab] | 5.8[c] |
| 100 + 40 N*ur ear emerg. | 11.5[b] | −0.4[a] | −0.4[a] | 10.7[b] | 1.8[c] | 0.4[bc] | 0.0[b] | 2.3[c] | 4.3[c] | 3.6[b] | 0.5[a] | 3.8[c] | 4.6[c] | 1.0[bc] | 0.1[b] | 5.7[c] |
| MSD | 6.2 | 2.0 | 3.1 | 7.7 | 2.4 | 0.2 | 0.1 | 2.3 | 2.3 | 2.3 | 1.8 | 2.0 | 6.0 | 0.5 | 0.2 | 5.9 |

1989


TOTAL NITROGEN IN FRACTIONS
FRACTION 1
FRACTION 2
FRACTION 3
FRACTION 4
NITROGEN IN FRACTIONS mg/g DM
TOTAL NITROGEN
GRAIN N (ANCA-MS)
10
9
8
7
6
5
4
3
2
1
30
20
10
1 2 3 4 5 6 7
TREATMENT
15N-LABELLED
UNLABELLED

1990


TOTAL NITROGEN IN FRACTIONS
FRACTION 1
FRACTION 2
FRACTION 3
FRACTION 4
NITROGEN IN FRACTIONS mg/g DM
TOTAL NITROGEN
GRAIN N (ANCA-MS)
10
9
8
7
6
5
4
3
2
1
30
20
10
1 2 3 4 5 6 7
TREATMENT

1.9 % in 1987, 47.1—53.8 % in 1988, 8.2—26.4 % in 1989 and 5.7—27.0 % in 1990. Top dressing of nitrate resulted in higher recovery of labelled nitrogen as inorganic nitrogen than the spring application of ammonium nitrate in 1987 and 1989, but to a lower recovery in 1990. In 1987, the total amounts and the differences were, however, small. In 1988, there were no statistically significant differences in this respect. The recovery of labelled urea nitrogen as inorganic nitrogen was lower than that of top dressed nitrate nitrogen.

### 5.3.4. Protein fractions in the grain and $^{15}$N-labelled nitrogen in the fractions

On average, 95.5 % and 101.1 % of the total nitrogen determined by the Roboprep-CN analyser in the grain yields of 1989 and 1990, respectively, was recovered by the fractionation procedure. The correlation between the two methods was slightly poorer, 0.7412***, for the grain of 1989 and better, 0.9730***, for 1990. The figures for the $^{15}$N-labelled fertilizer were 92.9 % and 0.9801*** as well as 97.8 % and 0.9969***, respectively.

There was no effect of the time of application or the form of nitrogen fertilizer on the protein content of the grain or the protein fractions in the grain (Fig. 15). The only statistically significant difference was that between the unfertilized and fertilized treatments. The highest increases in nitrogen content in the grain by fertilizer application were found in fractions 2 and 3. Also fraction 1 was statistically significantly increased, but less than fractions 2 and 3. There was no effect of fertilizer application on the nitrogen content in fraction 4.

Like in the pot experiment, the percentage of $^{15}$N-labelled nitrogen in a certain fraction of the total $^{15}$N-labelled nitrogen in the grain was in general almost equal to the corresponding percentage of total nitrogen in the fraction of total nitrogen in the grain (Table 23). Only in the yield of 1989 were there some slight differences between the percentages of unlabelled and labelled nitrogen of the respective grain total nitrogen, especially in fractions 2 and 4. The lower recovery of the nitrogen applied as urea also reflected as a lower recovery in the grain protein fractions.

The ratio between the fractions 2 and 3 was not affected by any of the treatments (Table 24). The corresponding ratio for the $^{15}$N-labelled nitrogen was not affected by the treatments either.

The amount of non-protein nitrogen in the grain of 1989 and 1990 was about 3 mg/g DM and 2 mg/g DM respectively (Fig. 16). This was 10—12 % and 8 % of the total nitrogen in the grain and about 41—48 % and 33—37 % of the fraction 1 protein nitrogen in the grain for the years in question, respectively. The corresponding proportions for the $^{15}$N-labelled nitrogen were slightly less, 7—8 % and 7 % for the total N in grain and 32—36 % and 33—34 % for the fraction 1 protein in the grain of

Fig. 15. The effect of time of application and the form of nitrogen fertilizer on amount of nitrogen in the protein fractions soluble in salt solution (fraction 1), aqueous ethanol (fraction 2), aqueous propanol — dilute acetic acid — mercaptoethanol (fraction 3), the insoluble residue (fraction 4) and the sum of the fractions and on the amount of $^{15}$N-labelled nitrogen in the fractions in the field experiment in 1989 and 1990.

Treatments:
1. unfertilized
2. 100 kg/ha unlabelled ammonium nitrate N at sowing

Treatments 3—7 100 kg/ha unlabelled ammonium nitrate at sowing plus
3. 40 kg/ha labelled ammonium nitrate N at sowing
4. 40 kg/ha labelled nitrate N at tillering
5. 40 kg/ha labelled nitrate N at ear emergence
6. 40 kg/ha labelled urea N at tillering
7. 40 kg/ha labelled urea N at ear emergence

Table 23. The effect of time of application and the form of nitrogen fertilizer on the proportional amounts of nitrogen and $^{15}N$-labelled nitrogen in the grain in the field experiment. * = $^{15}N$-labelled fertilizer. The results within the same fraction and same column followed by the same letter do not differ statistically significantly according to Tukey's test (P = 0.05)

| Fraction/ treatment | Year 1989 | | | Year 1990 | | |
|---|---|---|---|---|---|---|
| | Nitrogen % of total nitrogen in grain | $^{15}N$-lab. N % of $^{15}N$-lab. nitrogen in grain | $^{15}N$-lab. N % of total N in fraction | Nitrogen % of total nitrogen in grain | $^{15}N$-lab. N % of $^{15}N$-lab. nitrogen in grain | $^{15}N$-lab. N % of total N in fraction |
| FRACTION 1 | | | | | | |
| Unfertilized | 24.9[a] | — | — | 24.5[a] | — | — |
| 100 kg/ha N in spring | 23.4[a] | — | — | 22.8[b] | — | — |
| » +40 N*, spring | 22.9[a] | 21.6[a] | 14.8[a] | 21.7[c] | 21.4[a] | 19.4[a] |
| » +40 N*, tillering | 22.9[a] | 20.4[a] | 14.6[a] | 22.5[bc] | 21.6[a] | 19.0[a] |
| » +40 N*, ear emergence | 23.5[a] | 20.5[a] | 14.4[a] | 22.3[bc] | 21.3[a] | 20.7[a] |
| » +40 N*, urea, tillering | 23.1[a] | 20.8[a] | 5.7[c] | 22.0[bc] | 21.2[a] | 12.7[b] |
| » +40 N*, urea, ear emergence | 23.4[a] | 21.1[a] | 10.7[b] | 22.1[bc] | 21.4[a] | 13.8[b] |
| FRACTION 2 | | | | | | |
| Unfertilized | 28.9[b] | — | — | 30.4[b] | — | — |
| 100 kg/ha N in spring | 31.5[a] | — | — | 33.3[a] | — | — |
| » +40 N*, spring | 31.9[a] | 34.5[b] | 16.9[a] | 34.1[a] | 34.4[a] | 19.9[a] |
| » +40 N*, tillering | 31.7[a] | 35.6[ab] | 18.3[a] | 33.6[a] | 34.4[a] | 20.3[a] |
| » +40 N*, ear emergence | 31.6[a] | 36.3[a] | 18.8[a] | 33.2[a] | 34.2[a] | 22.3[a] |
| » +40 N*, urea, tillering | 31.8[a] | 35.3[ab] | 7.0[c] | 33.8[a] | 34.7[a] | 13.5[b] |
| » +40 N*, urea, ear emergence | 31.5[a] | 34.9[ab] | 13.2[b] | 33.2[a] | 34.5[a] | 14.8[b] |
| FRACTION 3 | | | | | | |
| Unfertilized | 24.5[b] | — | — | 24.4[b] | — | — |
| 100 kg/ha N in spring | 26.4[a] | — | — | 27.2[a] | — | — |
| » +40 N*, spring | 26.6[a] | 26.6[b] | 15.7[ab] | 27.4[a] | 27.8[a] | 20.0[a] |
| » +40 N*, tillering | 27.3[a] | 28.8[a] | 17.2[a] | 27.1[a] | 27.8[a] | 20.4[a] |
| » +40 N*, ear emergence | 26.5[a] | 28.1[ab] | 17.4[a] | 27.1[a] | 27.9[a] | 22.3[a] |
| » +40 N*, urea, tillering | 26.6[a] | 27.7[ab] | 6.6[c] | 27.2[a] | 27.7[a] | 3.4[b] |
| » +40 N*, urea, ear emergence | 26.6[a] | 27.5[ab] | 12.4[b] | 27.4[a] | 27.7[a] | 14.4[b] |
| FRACTION 4 | | | | | | |
| Unfertilized | 21.6[a] | — | — | 20.7[a] | — | — |
| 100 kg/ha N in spring | 18.7[b] | — | — | 16.7[b] | — | — |
| » +40 N*, spring | 18.7[b] | 17.3[a] | 14.5[a] | 16.8[b] | 16.5[a] | 19.3[a] |
| » +40 N*, tillering | 18.0[b] | 15.1[c] | 13.7[a] | 16.9[b] | 16.2[a] | 19.0[a] |
| » +40 N*, ear emergence | 18.4[b] | 15.1[c] | 13.4[ab] | 17.4[b] | 16.6[a] | 20.6[a] |
| » +40 N*, urea, tillering | 18.5[b] | 16.2[b] | 5.5[c] | 17.1[b] | 16.4[a] | 12.7[b] |
| » +40 N*, urea, ear emergence | 18.4[b] | 16.5[ab] | 10.7[b] | 17.2[b] | 16.3[a] | 13.5[b] |

Table 24. The effect of time of application and form of nitrogen fertilizer on the ratio of nitrogen and $^{15}N$-labelled nitrogen in the grain protein fractions 2 and 3 in the field experiment. * = $^{15}N$-labelled fertilizer. The results within the same column followed by the same letter do not differ statistically significantly according to Tukey's test (P = 0.05)

| Time of application | Year 1989 | | Year 1990 | |
|---|---|---|---|---|
| | 2/3-ratio total N | 2/3-ratio $^{15}N$-lab. N | 2/3-ratio total N | 2/3-ratio $^{15}N$-lab. N |
| Unfertilized | 1.20[a] | — | 1.25[a] | — |
| 100 kg/ha N in spring | 1.21[a] | — | 1.22[a] | — |
| » +40 N*, spring | 1.21[a] | 1.31[a] | 1.25[a] | 1.24[a] |
| » +40 N*, tillering | 1.18[a] | 1.25[a] | 1.24[a] | 1.24[a] |
| » +40 N*, ear emergence | 1.21[a] | 1.31[a] | 1.22[a] | 1.23[a] |
| » +40 N*, urea, tillering | 1.20[a] | 1.28[a] | 1.24[a] | 1.25[a] |
| » +40 N*, urea, ear emergence | 1.20[a] | 1.28[a] | 1.21[a] | 1.25[a] |

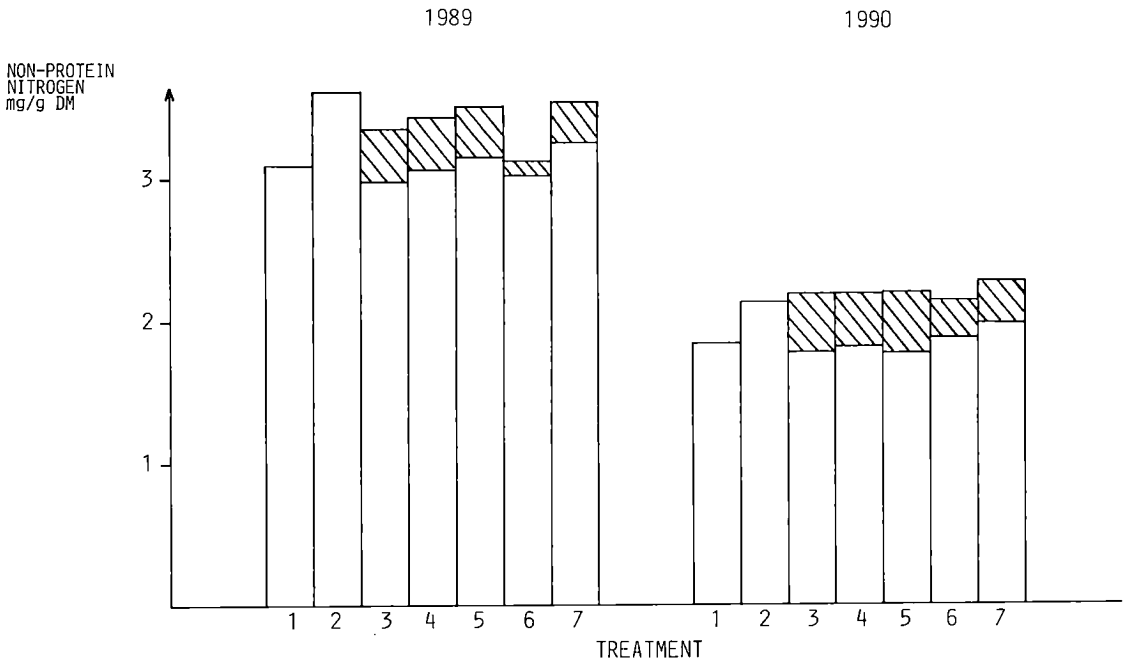



Fig. 16. The effect of time of application and form of nitrogen on the content of non-protein nitrogen in the grain and on the amount of $^{15}N$-labelled nitrogen in the non-protein nitrogen in the field experiment. The treatments 1—7 are the same as in figure 15.

Table 25. The effect of time of application and form of nitrogen fertilizer on the proportional amounts of non-protein nitrogen and $^{15}N$-labelled non-protein nitrogen in the grain in the field experiment. * = $^{15}N$-labelled fertilizer. The results within the same fraction and same column followed by the same letter do not differ statistically significantly according to Tukey's test (P = 0.05)

| Time of application | % of total N in grain | % of N in fraction 1 | % of $^{15}N$-lab. N in grain | % of $^{15}N$-lab. N in fraction 1 | $^{15}N$-lab. % of non-protein N |
|---|---|---|---|---|---|
| Year 1989 | | | | | |
| Unfertilized | 11.9[a] | 47.2[a] | — | — | — |
| 100 kg/ha N in spring | 11.3[a] | 47.7[a] | — | — | — |
| » + 40 N*, spring | 10.4[a] | 45.0[a] | 7.8[a] | 36.0[a] | 12.1[a] |
| » + 40 N*, tillering | 10.6[a] | 45.7[a] | 6.9[a] | 33.6[a] | 11.0[ab] |
| » + 40 N*, ear emergence | 10.7[a] | 44.6[a] | 6.8[a] | 32.9[a] | 10.9[ab] |
| » + 40 N*, urea, tillering | 9.6[a] | 40.8[a] | 6.6[a] | 31.8[a] | 4.5[c] |
| » + 40 N*, urea, ear emergence | 10.9[a] | 46.0[a] | 7.1[a] | 33.7[a] | 8.0[b] |
| Year 1990 | | | | | |
| Unfertilized | 8.2[a] | 33.4[a] | — | — | — |
| 100 kg/ha N in spring | 7.6[a] | 3.6[a] | — | — | — |
| » + 40 N*, spring | 7.6[a] | 35.1[a] | 7.3[a] | 34.3[a] | 19.0[a] |
| » + 40 N*, tillering | 7.9[a] | 35.1[a] | 7.0[a] | 32.7[a] | 17.7[a] |
| » + 40 N*, ear emergence | 8.0[a] | 35.8[a] | 7.0[a] | 32.9[a] | 19.1[a] |
| » + 40 N*, urea, tillering | 7.7[a] | 35.3[a] | 6.9[a] | 32.5[a] | 11.7[b] |
| » + 40 N*, urea, ear emergence | 8.2[a] | 37.2[a] | 7.1[a] | 33.0[a] | 12.2[b] |

1989 and 1990, respectively (Table 25). About 5—12 % and 12—19 % of the non-protein nitrogen was $^{15}$N-labelled fertilizer nitrogen in the grain of 1989 and 1990, respectively. The only statistically significant difference in the effect of the treatments on the non-protein nitrogen in the grain was in the proportion of the $^{15}$N-labelled nitrogen of the non-protein nitrogen, where the recovery of $^{15}$N from urea spraying was lower, reflecting a lower recovery of urea nitrogen, in general, rather than anything else.

## 5.4. Discussion

### 5.4.1. Accuracy of the results

The precision of the mass spectrometer is better than 0.001 atom % $^{15}$N. The possible sources of errors in the methods of pretreatment of the samples for mass spectrometric determination have already been discussed in the methods section. Avoiding cross-contamination between the samples is the most important measure, after one is sure that the methods of analysis are accurate. This is done by treating the samples in order of proposed ascending enrichment of $^{15}$N and cleaning the tools between each treatment thoroughly. After these measures the accuracy of the methods of $^{15}$N analysis is so high that it can only cause a minor error in the results.

Spatial variability is the main problem in the $^{15}$N technique (PRUDEN et al. 1985b, SAFFIGNA 1987). Band placement of nitrogen fertilizers involves great spatial variability of inorganic nitrogen and $^{15}$N-labelled nitrogen in soil. Also the natural heterogeneity in inorganic nitrogen content in soil is great (LINDEN 1981). The dry conditions in 1988, in particular, increased this spatial variability, which reflected in the results, although many subsamples were taken from the plots. The improved sampling methods for 1989 and 1990 eliminated some of these problems.

The enrichment of $^{15}$N-labelled nitrogen in the fertilizer applied should be high enough to find the differences, especially, between the treatments and the soil background enrichment of $^{15}$N. The enrichment of 5 atom % used on clay soil containing 0.22—0.27 % nitrogen in topsoil and 0.04—0.09 % in subsoil was not high enough to give accurate results in 1987—1989. This enrichment has been used in many studies on soils with about the same nitrogen content as in the present study. The low enrichment of nitrogen applied reduced the accuracy of the results of recoveries of total $^{15}$N-labelled nitrogen in soil, especially in 1987, when the amount of residual nitrogen was small. The accuracy is less for the results of subsoil than those of topsoil.

Also the low enrichment of urea nitrogen reduced the accuracy of the results. These defects in accuracy of recovery of labelled nitrogen in soil total nitrogen are also reflected in the results of total balance of fertilizer nitrogen. The differences were often statistically insignificant.

In 1990, the enrichment of the fertilizer applied was about 10 atom % and the total nitrogen content in the top soil was lower, 0.20 %. So these results are more accurate. The enrichment of $^{15}$N in the fertilizers was, in all cases, high enough to get accurate results of the recovery of labelled nitrogen in plants and as soil inorganic nitrogen.

### 5.4.2. Recovery of $^{15}$N-labelled fertilizer

The range of recovery of $^{15}$N-labelled nitrogen in the crops of the present study was 15—69 %. The lower end of the range was below the lowest values of 27 % reported by DRES-

SEL and JUNG (1990) in their review. The highest values of the present study agree with their highest values of 70 %. The recoveries for individual years reflected the moisture conditions prevailing in these years. The lowest recoveries were obtained in the exceptionally dry year of 1988, and the highest recoveries in the exceptionally wet year of 1987.

The effect of time of application of the top dressing of nitrogen fertilizer on the recovery of $^{15}$N-labelled nitrogen was in the rainy year of 1987 equal to the results obtained by RIGA et al. (1988), DESTAIN et al. (1990a) and DESTAIN et al. (1990b) in winter wheat in rainy years on a silty soil in Belgium. RIGA et al. (1988) noticed that totally 100 kg/ha nitrate nitrogen given as top dressings at the end of tillering, heading and beginning of flowering were recovered 54.6 %, 67.8 % and 69.9 %, respectively, i.e. the better the later the top dressing was applied. The amounts of labelled nitrogen unaccounted for were 26.6 %, 22.3 % and 18.6 %, respectively. Also this result, earlier applications yielding greater losses, agreed with the results of the present investigation in 1987. However, the differences in the present study were not statistically significant. RIGA et al. (1988) and DESTAIN et al. (1990b) suggested that the losses were caused by denitrification, because leaching was not probable in the prevailing moisture conditions.

In 1988, the results were opposite, the highest recoveries being obtained from the earlier applications. In 1989 and 1990 there were not great differences in the time of application for the recovery of $^{15}$N-labelled nitrogen.

A large series of experiments was arranged by the FAO (1974) in six countries, Egypt, Brazil, India, Italy, Pakistan and Turkey. The results showed that top dressing part of the nitrogen later in the growing season gave a higher recovery of $^{15}$N-labelled nitrogen in all the other countries except Italy, where there was a dry period after application of the top dressing. The investigators concluded that top dressing part of the nitrogen during the growing season results in a higher recovery of nitrogen in absence of drought after application of the fertilizer. However, no constituent interaction with water regime and time of application was discovered in the experiments especially designed to study this issue.

In the experiments of the FAO (1974), LEITCH and VAIDYANATHAN (1983), YONEYAMA (1983) and RIGA et al. (1988), a greater proportion of fertilizer nitrogen was recovered in grain and a smaller proportion in straw, when nitrogen was applied later in the growing season. In the present experiments, this phenomenon was only noticed in the pot experiment, but not in the field experiments. This was presumably due to the fertilizer nitrogen applied later during the growing season possibly being accumulated less in the structural nitrogen containing compounds of the straw than the nitrogen applied at earlier growth phases.

The recovery of the $^{15}$N-labelled nitrogen in the roots was 2—5 % in the pot experiment and 3—6 % in the field experiment in 1989. In the other years in the field experiments the roots were not separated from the soil, but the result of soil total nitrogen analysis was assumed to contain also the roots. In the pot experiments of JAAKKOLA and YLÄRANTA (1985a), barley roots contained 3—11 % and in the pot experiments of YLÄRANTA and JAAKKOLA (1985), 8—15 % of the $^{15}$N-labelled nitrogen applied. VANCLEEMPUT et al. (1981) noticed in a field experiment that only 2 % of the $^{15}$N-labelled nitrogen applied was recovered in the roots. So in most cases the amount of nitrogen in roots is low and cannot cause great errors in the total balance of $^{15}$N-labelled nitrogen fertilizer, even if the roots are not separated from the soil.

### 5.4.3. Probable losses of nitrogen

Actual measurements of the losses of nitrogen were outside the scope of the present study.

However, some assumptions based on literature of the probable losses of nitrogen can be made.

The most probable reasons of the known possible losses of nitrogen from the soil-plant system in the present study are leaching, denitrification and volatilization of ammonia from the canopy. Volatilization of ammonia from the soil is not presumable, because the pH of the soil was not very high (6.2—6.7) and nitrate nitrogen was used for the top dressing of nitrogen fertilizer.

*Denitrification and leaching*

The greater losses from the earlier applications, and especially from the application at sowing time in 1987, may be caused by leaching or denitrification. The amount of fertilizer nitrogen was, however, not very large in the deeper soil layers (60—90 cm), not even in the inorganic form, which may mean that leaching is less probable. The enrichment of the $^{15}N$-labelled nitrogen applied was probably not, however, high enough to show this kind of differences accurately in 1987.

Leaching as an explanation of the losses in 1988 is suggested by the fact that the losses were greatest from the later applications and the fertilizer may have immobilized from the earlier applications before the first rain after the long drought period. The nitrogen applied later can be assumed to have been mostly in inorganic form and so more easily leacheable. The precipitation was high in the latter half of July. Almost all of the total precipitation of 128 mm occurred after 15 July. So great leaching losses were possible. However, if this explanation is valid, the amount of $^{15}N$-labelled nitrogen in the deeper layers of the soil should be higher as a consequence of later fertilizer applications than after earlier applications, which was not the case. However, again in 1988 the enrichment of the $^{15}N$ in the fertilizer was perhaps not high enough for accurate results, although it was higher than in 1987.

Many investigations have shown that fertilizer nitrogen has not to any great extent leached down below the top layer of the soil by harvesting of the crops (RIGA et al. 1980, STREBEL et al. 1980, RECOUS et al. 1988a, RIGA et al. 1988, DESTAIN et al. 1990b, DRESSEL and JUNG 1990) even in wet conditions (CRASWELL and STRONG 1976). This fact has generally been considered to rule out the possibility of leaching of fertilizer nitrogen before harvest.

JAAKKOLA and YLÄRANTA (1985b) noticed in lysimeter experiments that only about 1 % of the $^{15}N$-labelled nitrogen applied to an irrigated barley crop was recovered as leaching from a clay soil during two years. BERGSTRÖM (1987) obtained equal results in three-year lysimeter experiments in Sweden. KJELLERUP and DAMKOFOED (1983) noticed in lysimeter experiments that 5 % of the $^{15}N$-labelled nitrogen fertilizer had leached in three years time after application. So, when comparing these results with the above results, leaching of 13 and 14 kg/ha of nitrogen in 1987 and 1988, respectively, seems unlikely. Also RIGA et al. (1980) drew the same conclusion based on literature.

In the field experiment, denitrification was possible in 1987, because the growing season was rainy and the low oxygen conditions favouring denitrification were possible. The high precipitation in the late July in 1988 may also have caused low oxygen conditions in the soil, which may have led to denitrification losses. This can explain a great proportion of the losses. For instance COLBOURN et al. (1984) estimated that more than 30 % of fertilizer nitrogen was lost in three weeks after application in spring after a precipitation of 60 mm.

In the pot experiment, part of the losses of the present study may have been due to denitrification. Although the soil was only slightly compacted sandy soil, intensive watering may have caused oxygen deficient conditions in the soil from time to time. However, YLÄRANTA and JAAKKOLA (1985) could only show 1.1—1.3 % total losses of $^{15}N$-labelled nitrogen from an uncompacted sandy soil in an

experiment where denitrification was investigated. So, denitrification is not a very likely explanation for the losses of $^{15}N$-labelled nitrogen in the pot experiment.

*Gaseous losses of nitrogen from the plants*

One possible explanation for the fertilizer nitrogen unaccounted for from the later applications in 1988 and in the pot experiment is the gaseous loss especially in the form of ammonia from the leaves of the senescing plants. WETSELAAR and FARQUHAR (1980) showed in their literature review that differences as great as 70 kg/ha (35 %) in the nitrogen content between the maximum content and harvest have been noticed (DAIGGER et al. 1976). Nitrogen can be lost from the plant tops especially by translocation to the roots, leaching from the leaves or volatilization of gaseous compounds, e.g. ammonia, some other amines, $N_2$, nitrogen oxides, hydrogen cyanide and some alkaloids from the leaves.

STUTTE and WEILAND (1978) estimated in their field measurements that 45 kg/ha was lost from a soy bean crop to the atmosphere during the growing season. HARPER et al. (1987) noticed that 21 % of the fertilizer nitrogen was lost by volatilization of ammonia from a winter wheat crop. Of the fertilizer nitrogen, 11 % was lost after fertilizer application and 10 % between anthesis and maturity from the senescing leaves. In the pot experiment of PARTON et al. (1988), volatilization of ammonia from spring wheat unit leaf area was quite constant, 60—120 ng/m$^2$/s, from ear emergency to onset of senescing period, but volatilization increased in the senescing period to 200—300 ng/m$^2$/s.

RECOUS et al. (1988b) noticed that the content of $^{15}N$-labelled fertilizer nitrogen in winter wheat had decreased at harvest 19 % from the maximum content of the crop, when nitrate nitrogen had been used as fertilizer. No corresponding decrease was noticed, when ammonium or urea nitrogen was used as fertilizer, but their maximum uptake was lower, and so at harvest the recovery of all these three nitrogen forms was almost equal. They concluded that the losses of nitrate fertilizer from the plant were probably caused by volatilization of ammonia from the plant or leaching of nitrogen compounds from the leaves to the soil. The lower uptake of ammonium and ammonium forming nitrogen was due to higher immobilization of ammonium nitrogen to the soil microbes compared to nitrate nitrogen as also noticed by DRESSEL and JUNG (1990) and RECOUS and MARY (1990).

CRASWELL and MARTIN (1975) observed that a drought period at anthesis and after it resulted in losses of $^{15}N$-labelled nitrogen from the plants. They could not show with certainty whether the losses were caused by volatilization of ammonia from the leaves or by translocation of nitrogen from the leaves to the roots of the plants. They concluded that the unexplained losses of nitrogen have often in literature been suggested to have been caused by denitrification, even in rather dry conditions. They concluded that denitrification is remarkable only when the soil is saturated by water and suggest that the gaseous losses of nitrogen should be considered more carefully when the nitrogen balance of the soil-plant system is investigated. CRASWELL and STRONG (1976), however, were not able to repeat the result in experiments where the plants had two moisture treatments, dry and wet, during the whole growing season.

YONEYAMA (1983) noticed losses of nitrogen from the crops only after fertilizer applications at the beginning of the growing season of spring wheat in a pot experiment, and the total losses were 4 % of the applied $^{15}N$-labelled nitrogen. SMITH et al. (1984) and SCHJØRRING et al. (1989) reported a decline of fertilizer nitrogen after anthesis of highly fertilized barley crops.

In the present study, the plant samples taken at anthesis about one week after ear emergence

in 1988 showed that the plants receiving the total amount of nitrogen in spring had by that stage taken up most of the nitrogen (87 %) they contained at harvest (Table 20). From the application at tillering the plants had taken up 50 % of the total content at harvest. From the application at ear emergence the plants had hardly taken up any nitrogen. The first rain after a long drought period after about ten days from this sampling can be assumed to have started the uptake of nitrogen, resulting in a high nitrogen content in the plant, but an early senescence caused by a new drought period probably resulted in volatilization of ammonia from the crop.

Late application of fertilizer increases the content of inorganic nitrogen compounds, especially ammonium, in the plant, and a senescing plant is no longer able to assimilate all of it (WETSELAAR and FARQUHAR 1980). The losses of nitrogen from the crop have been greatest when the nitrogen content in the plant is high in the senescing period, e.g. after intensive application of nitrogen fertilizer.

In the case of late nitrogen application in the present experiments these two phases of the high possibility of gaseous losses were overlapping. So, gaseous losses from the plants probably explained the losses noticed in some cases. However, actual measurements to prove this hypothesis were outside the scope of the present study.

### 5.4.4. Recovery of urea nitrogen

The recovery of urea in the crop was in the present study 16—41 %, which was only 40—70 % of that of the soil applied nitrate nitrogen at the same growth stages. The soil analyses showed that in two of the four cases this difference between urea and soil applied nitrate nitrogen was recovered in the soil and in two cases not. POWLSON et al. (1987) recovered 62 % (45—77 %) of the 30 kg/ha of nitrogen applied as urea to a winter wheat crop, half before anthesis and the other half after anthesis. POWLSON et al. (1989) recovered at harvest 70 % of the nitrogen applied as urea (40 kg/ha) at anthesis. The recovery was slightly less (64 %/58 %) for the earlier (GS 39) and later (GS 73) applications. POULTON et al. (1990) recovered both the soil and foliar-applied nitrogen equally in the crop (about 50 %) for the corresponding applications. Less nitrogen originating from urea was recovered in soil (1—11 %) than from the soil applied nitrogen (25 %) suggesting greater losses of urea nitrogen from the crops, e.g. in gaseous forms.

One possible explanation for the lower recovery of urea nitrogen is the volatilization of gaseous ammonia from the leaves. However, no severe scorching of the leaves was observed in any of the crops after spraying. The fact that in three out of four cases 25—30 % and in one case about 60 %, of the total urea recovered in the crops was recovered at anthesis suggests that in these three cases more than half of the urea nitrogen applied circulated through the soil to the plants. This could result in higher immobilization and residual nitrogen in the soil than of the soil applied nitrogen (RECOUS et al. 1988a), which in fact was the case in two of the cases.

A third possibility is the excretion of urea nitrogen applied foliarly from the roots to the soil resulting in a lower recovery of urea nitrogen in the plants and a higher recovery in the soil (WETSELAAR and FARQUHAR 1980). HUNDT et al. (1990) noticed that about 10 % of the foliar-applied urea nitrogen was translocated to the roots, which can also in part explain the higher recovery in the soil, because the roots were included in the soil in these experiments. However, the same may be true of the soil applied nitrogen.

The plant cover of the ground is thinner in the Finnish conditions compared to British, and more of the urea may thus end onto the soil surface. Also the shorter growing season and faster development of the plants may lead to

higher gaseous losses from the crops compared to the more southern latitudes. This may explain the differences in the results of the present study compared to those of above mentioned British results.

Finally, the technique of urea application can be attributed for the lower recovery (POWLSON et al. 1989). The nozzles may give various amounts of liquid and the speed of the spraying may not be right. However, these sources of error were carefully minimized when spraying the crops. The defects in the technique can only have a minor significance and obviously cannot explain the very much lower recoveries of urea nitrogen compared to soil applied nitrogen, for at least in two of the cases the lower recovery of nitrogen from sprayed urea in the above ground parts of the crops was recovered in the soil.

### 5.4.5. Extractable inorganic nitrogen in soil at harvest

About 29—35 %, 49—71 %, 38—49 % and 34—42 % of the $^{15}$N-labelled nitrogen applied was retained in the soil at harvest on the plots receiving ammonium nitrate in spring or nitrate as top dressing in 1987, 1988, 1898 and 1990, respectively. About 68—95 %, 76—81 %, 78—87 % and 92—99 % of this nitrogen was in the upmost 25 cm soil layer, respectively. The amounts of labelled inorganic nitrogen from the total amount applied recovered in the 0—25 cm layer in these experiments were 0.6—1.6 %, 32.6—42.3 %, 4.7—17.6 % and 13.9—25.3 % in 1987, 1988, 1989 and 1990, respectively. The corresponding figures for the 0—90 profile were 0.9—1.9 %, 47.1—53.9 %, 8.2—26.4 % and 15.9—27.0 %.

MACDONALD et al. (1989) noticed that on average 17 % (range 7—36 %) of the spring applied labelled nitrogen (47—234 kg/ha) remained in the 0—23 cm soil layer at harvest. The amount of $^{15}$N-labelled inorganic nitrogen averaged 1.3 % (0.4—3.6 %) of the fertilizer applied. MACDONALD et al. (1990) recovered 21 % of 224 kg/ha labelled nitrogen applied to winter wheat in spring in the 0—100 cm profile at harvest. The amount of inorganic $^{15}$N-labelled nitrogen corresponded to 2.5 % of the amount applied. The fertilizer practices in these two papers were, however, different from those in the present study, the total application being labelled instead of only the split portion as was the case in the present study.

So, the recoveries of $^{15}$N-labelled nitrogen recovered in inorganic form at harvest were higher in the present study compared to above mentioned studies in all the years, except 1987. This can be explained by the dry growing seasons of 1988—90 leading to less immobilization during the growing season. A flush of soil mineral nitrogen and perhaps some recently immobilized fertilizer nitrogen before harvest, when the soil was rewetted by the rains also led to this. In addition, the very high recovery of the applied fertilizer in 1988 can be explained by the poor crop uptake of nitrogen. The results of 1988 may not be quite reliable, and the behavior of nitrogen in these very dry conditions would need further investigations.

Of the residual inorganic nitrogen in the 0—90 cm profile 80—99 % and in the 0—25 cm layer 76—98 % was unlabelled. This result agrees with the results of MACDONALD et al. (1989), who found 79—98 % of the total residual inorganic nitrogen in the 0—25 cm layer as unlabelled, and the results of MACDONALD et al. (1990), who found 89 % of residual nitrogen in the 0—100 cm layer as unlabelled. Again, the labelled portion of the total amount of nitrogen applied was greater in their studies than in the present study.

The differences in the total residual nitrogen could not be explained by the differences in the labelled inorganic nitrogen, although in 1988 about 70—95 % of the total labelled residual nitrogen was recovered as labelled inorganic nitrogen. In 1987, 1989 and 1990 the corresponding recoveries were 6—16 % 22—55 %

and 47—59 %, respectively, for the treatments, except for urea spraying. Compared to the top dressings, a smaller proportion (11—22 %) of labelled residual nitrogen retained in the soil after urea spraying was recovered as inorganic nitrogen. This can be explained by higher immobilization of the ammonium nitrogen formed from the urea falling on the ground as shown by e.g. RECOUS et al. (1988a), or by excretion of the urea originating nitrogen from the roots.

The results of residual mineral nitrogen in soil from the present field experiment using $^{15}N$-labelled fertilizers on microplots agree quite well with the results of the larger field experiment 'Split application of nitrogen fertilizer to spring wheat' in 1987 and 1988 (ESALA 1990). The total amounts of inorganic nitrogen were high especially in 1988, but also in 1989—90, compared to the results of SIPPOLA and YLÄRANTA (1985), MACDONALD et al. (1989) and MACDONALD et al. (1990). This can be explained by the dry growing seasons as shown by LINDEN (1983). A dry former part of the growing season leading to a low yield and movement of nitrate nitrogen to the very top of the soil (KAILA and HÄNNINEN 1961, KAILA and ELONEN 1971) in connection with a flush of inorganic nitrogen from the soil caused by remoistening of the soil by rain (LINDEN 1983) as in 1988, 1989 and 1990 in the present study lead to high amounts of residual mineral nitrogen in soil.

The result of 1988 that spring application would lead to higher amounts of residual inorganic nitrogen in soil may, however, be incorrect. This result concerns mainly the unlabelled portion of inorganic nitrogen and not the labelled portion. However, the portion of residual labelled nitrogen as inorganic nitrogen is high, 70—95 %. Even the roots may contain about 5 % of the nitrogen applied as shown e.g. in the pot experiment and in the field experiment in 1989.

### 5.4.6. Protein fractions in the grain and $^{15}N$-labelled nitrogen in the fractions

In the pot experiment the gliadins and glutenins and the residual proteins of the grain were increased by extra nitrogen, especially by the later applications. No corresponding increases were found in the field experiment by the timing of application. The amounts of the gliadin and glutenin fractions were, however, higher in the fertilized treatments compared to the unfertilized treatments. The increased amounts of these fractions can be explained by an increase in the endosperm proteins generally observed by nitrogen fertilizer (ABROL et al. 1971, DUBETZ et al. 1979, DOEKES and WENNEKES 1982). Such changes in the proportions of the fractions have been shown to increase the loaf volume (HOSENEY et al. 1969, DOEKES and WENNEKES 1982).

The effect of the time of application of the nitrogen fertilizer on the fate of $^{15}N$-labelled fertilizer in the protein fractions of the grain has previously been reported by YONEYAMA (1983). He found that there was no difference in the contribution of $^{15}N$-labelled nitrogen taken up by wheat at different growth phases to the nitrogen in the protein fractions between the fractions. The results of the present study can be summarized correspondingly.

There was no indication, neither in the pot experiments, where the protein content was increased, or in the field experiments, where no such increases were found, that fertilizer nitrogen, even late applied, would be translocated more intensely to a certain fraction of protein formed at a certain growth stage. Inversely, the plant seems to circulate its nitrogen to a great extent (SIMPSON et al. 1983) and so the nitrogen sources utilized at different growth stages are equally translocated to the different protein fractions of the grain. However, it would be interesting to investigate, if the late applied extra nitrogen is translocated to different subunits of e.g. gliadins, as this could explain the dif-

ferences in the baking quality as discussed previously.

Also the assumption that late applied nitrogen would not be metabolized to proteins in the grain, but stored as non-protein nitrogen more pronouncedly as observed by FINNEY et al. (1957), could not be shown in these investigations. However, the very late application was only included in the pot experiment.

## 6. DISCUSSION AND CONCLUSIONS

The aim of the present study was to investigate the effect of split application of nitrogen fertilizer on the yield, quality, especially protein content and quality, and some agronomic properties of spring wheat, as well as the fate of $^{15}N$-labelled nitrogen fertilizer in the soil-plant system. Two issues of top dressing of nitrogen fertilizer, time of application and form of nitrogen in the fertilizer, were studied. The amount of fertilizer was 140 kg/ha, which was either applied as one dose in spring or split into two portions, 100 kg/ha applied in spring plus 40 kg/ha applied either at tillering or at ear emergence of the crops. The forms of nitrogen were ammonium nitrate, nitrate and urea which was either applied as granular or foliar.

The weather conditions of the experimental years were exceptional: the 1986, 1988, 1989 and 1990 summers, especially the early parts, were dryer than normal, while the 1987 summer was cool and rainy. The results are, however, quite well in agreement with those from the previous experiments on this subject in Finland. The experiments were arranged on clay soils, which are the most common soils in spring wheat cultivation in Southern Finland. How these results are applicable to, for instance, sandy soils, which are also found to some extent in spring wheat cultivation in Southern Finland would need further investigation. Also a different, e.g. lower, nitrogen fertilizer level, than the 140 kg/ha used in these experiments might give different results.

The two varieties, Luja and Heta, on the other hand, and Kadett, representing two different types, low yield, high protein and high yield, low protein, did not differ considerably in their reactions to the experimental treatments.

### 6.1. Time of application of nitrogen

According to the results of the present study and most of the previous studies, the highest yield is obtained by applying the total amount of nitrogen as one dose in spring. The yield increases obtained by top dressing of nitrogen at ear emergence in some investigations were not obtained in these experiments. Application of growth regulator to the spring fertilized crops increased the yield. The application of growth regulator to the top dressed plots was not, however, studied.

Splitting the fertilizer application increased the protein content of the grain. The application at ear emergence resulted in higher protein contents than the application at tillering. The yield increase obtained by growth regulator treatment decreased the protein content by 0.3 percentage units on average. In general,

the changes in protein contents by the timing of the application of nitrogen fertilizer were probably mostly affected by the changes in yield, because there were no statistically significant differences in grain nitrogen yield between the different treatments applying the corresponding amounts of nitrogen.

The baking quality of protein was not affected by the time of application of nitrogen fertilizer. The protein fractions 2 and 3, and to some extent 4, were increased with increasing protein content of the grain by top dressing of nitrogen in the pot experiment. These fractions were increased the more the later the top dressing. In some of the field experiments, where the proteins were fractionated and where no differences in protein content were found, there were no differences in the ratios of the protein fractions. No differences were found in the proportional amounts of $^{15}N$-labelled nitrogen from top dressed fertilizer and the unlabelled nitrogen from the basic spring application and soil derived nitrogen in the fractions of protein in the grain.

Lodging decreased statistically significantly, when part of the nitrogen dose was applied later. This influence was, however, so small that it does not have any great practical meaning in preventing lodging. The lower amount, 100 kg/ha, of nitrogen and, on the other hand, the growth regulator treatment decreased lodging more considerably. Falling number, test weight and thousand grain weight were not affected by the time of application of nitrogen fertilizer.

The pot experiment and field experiments with $^{15}N$-labelled fertilizer showed that in ample moisture conditions the highest recovery of fertilizer nitrogen in spring wheat is obtained by applying part of the nitrogen dose as top dressing at ear emergence. Application at that time also resulted in highest recovery of fertilizer nitrogen in grain. In field conditions, however, when the former part of the growing season was dry, band placing the total dose of nitrogen at sowing gave the highest recoveries of fertilizer nitrogen. In dry conditions the differences were, however, small and the recovery of fertilizer nitrogen was, in general, low.

In the present experiments it could not be shown that the late applied fertilizer nitrogen would be in larger amounts as inorganic nitrogen at harvest than the earlier applied nitrogen. More than 80 % of the inorganic nitrogen found in soil at harvest originated from the basic spring application or from the nitrogen mineralized from the soil. This observation is in agreement with the observations of MACDONALD et al. (1989) and MACDONALD et al. (1990) that a certain year's fertilizer nitrogen is of minor importance in the residual nitrogen in soil at harvest, although in their experiments a greater proportion of nitrogen was labelled than in the experiments of the present study. In dry years, however, the recovery of fertilizer nitrogen in the crops is low, and large amounts of fertilizer nitrogen, and soil derived nitrogen as well, may be found as inorganic nitrogen in the soil at harvest. This nitrogen is prone to leaching later, because there is no crop to take it up and there is more runoff of water in the autumn.

Many investigations have shown that in dry conditions prevailing in the few centimetres of the soil surface in the dry periods of some growing seasons, ammonium nitrogen is not nitrified. In these conditions nitrate nitrogen is translocated by the evaporating water to the same layer (KAILA and HÄNNINEN 1961, LINDEN 1983), where there is only very scanty root system in these conditions (KÄHÄRI and ELONEN 1969). All these phenomenona can limit the uptake of nitrogen by the plants, leaving more residual nitrogen to the soil that is prone to leaching. The effect of weather conditions, mainly moisture conditions, on the dynamics of fertilizer nitrogen and soil derived nitrogen should be investigated more thoroughly.

The leaching of fertilizer nitrogen by harvest of the crops was probably small both in a dry

and a wet growing season. A more probable explanation for the losses of nitrogen in a wet growing season is denitrification and on dry years volatilization of ammonia from the crops. Also denitrification was possible in the dry summers followed by a rainy period. Denitrification is, however, too often suggested as the reason for the unaccounted for nitrogen in the experiments made with $^{15}N$-labelled nitrogen. The gaseous losses of nitrogen from the crops, mainly as volatilization of ammonia, on the other hand, are not very largely investigated, but in many cases a clearly shown form of losses of nitrogen. So, these phenomena should be more investigated.

## 6.2. Form of fertilizer nitrogen for top dressing

The form of fertilizer nitrogen for top dressing did not affect the yield of the crops. The protein content in the grain was lower, when urea spraying was compared with the other three fertilizers tested: calcium ammonium nitrate and calcium nitrate and granular urea.

The form of fertilizer used for top dressing did not affect the results of the baking test. Baking tests could only be performed from the yields of two experimental years, because the other quality characters of the yield, especially falling number, were low in the other experimental years. So, the material for the baking tests was small. Urea spraying or late applications of nitrogen, in general, did not decrease the baking quality of the crops as noticed in some other investigations. The differences might be observed with a larger proportion of nitrogen and later applications of nitrogen for top dressing than was included in the experimental treatments in the present study.

The baking test used in the present study was probably not a sensitive enough method to find out the changes in the protein quality caused by top dressing of different forms of nitrogen. The changes should rather be investigated by determining the changes in the relative amounts of for instance the subunits of the gliadins and glutenins, which was not possible in the present study. Also the changes in the N/S-ratio of the grain and in the amounts of sulphur containing protein subunits should be investigated more, because the deterioration of the protein baking quality by top dressing of nitrogen fertilizers may be associated with an acute sulphur deficiency in relation to high nitrogen content at grain filling.

The recovery of $^{15}N$-labelled nitrogen from foliar-applied urea was lower than that of nitrate nitrogen top dressed or the spring applied ammonium nitrate nitrogen. The differences are probably explained by greater losses as volatilization of ammonia from the crops or by greater immobilization of the urea nitrogen falling on the soil surface. A relatively smaller amount of the $^{15}N$-labelled residual nitrogen in the soil was found as inorganic nitrogen compared to the other treatments. So, urea spraying can be presumed to cause less environmental problems by leaching, at least in the autumn following the growing season of application, but more probably problems related to ammonia emissions from the crops.

The economy of the different treatments affect most the decisions made by the farmer. The results of the present study suggest that an ample nitrogen application as one dose at sowing supplemented with growth regulator treatment when necessary gives the best economical result. The yield is still the major factor determining the economical result of the crop, and the premium paid for the protein

content should be severalfold to cover the yield decrease caused by splitting the nitrogen dose. Splitting the nitrogen application does not according to the results of the present study affect the other quality factors, falling number and test weight, paid to the farmer in Finland.

## 6.3. Means to increase the protein content and protein quality in spring wheat in Finland

The protein content of spring wheat is mostly dependent on weather conditions. The statistics of the Research Laboratory of the Grain Board of Finland from 1969 to the present show a year to year variation of 11.4 to 15.9 %, i.e. 4.5 percentage units in the average protein content of spring wheat. The year to year variation in the present study was 4.2 and 2.2 percentage units for Heta and 5.9 and 2.1 percentage units for Kadett for the treatment of 140 kg/ha nitrogen at sowing applied at Jokioinen and at Mietoinen, respectively. These year to year variations can be assumed to have been caused mainly by weather conditions.

A dry former part of the growing season leading to a low yield and movement of nitrate nitrogen to the very top of the soil (KAILA and HÄNNINEN 1961, KAILA and ELONEN 1971) in connection with a flush of inorganic nitrogen from the soil caused by moistening of the soil by rain (LINDEN 1983) together with the downward movement of the conserved nitrogen like in 1986, 1988, 1989 and 1990 in the present study result in high protein contents. Growing seasons with ample moisture conditions leading to high yields and some losses of nitrogen possibly by some leaching, but also denitrification and larger immobilization of fertilizer nitrogen lead to lower protein contents of the grain.

The difference in the average protein content of the Finnish varieties on the official list is 2.6 percentage units (KÖYLIJÄRVI and TALVITIE 1991). Some new varieties have been released in recent years in Finland yielding high protein content of good quality and a fair yield as well. The quality of the HMW glutenins in the Finnish spring wheat varieties is competitive with for instance to the good Canadian varieties (SONTAG et al. 1986, LUKOW et al. 1989).

Increasing nitrogen fertilizer doses can increase the protein content by 0.2—0.3 percentage units per each 10 kg/ha of extra nitrogen applied, and the yield as well. The fertilizer amounts applied for the spring wheat in Finland may be well below the economical optimum. However, increasing of risk of leaching of nitrate nitrogen and other environmental problems as well as the risk of lower falling number and higher harvesting and drying costs of the crop caused by the lodging do not justify increasing nitrogen fertilization to increase the protein content of the Finnish spring wheat.

According to the results of the present study, splitting the nitrogen fertilizer application would only give an average increase in protein content of 0.6 percentage units at the most, usually less, and the yield would decrease in the same connection. This does not give the farmer an economical means of modifying the protein content of the crop. In addition to that the year to year variation would be greater depending on the moisture conditions and the availability of the top dressed nitrogen. So, it cannot be recommended as a routine means of increasing the protein content of the Finnish spring wheat.

Weather conditions are the most important reason for the low protein content in the Finnish spring wheat in some years. They also cause most of the year to year variation. According to the results of the present study and most of the previous studies rate and timing of nitrogen application does not offer a great opportunity to increase the protein content and pro-

tein baking quality in Finnish spring wheat. The means for this should be searched from breeding better varieties and trying to persuade the farmers to choose these varieties.

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## SELOSTUS

### Jaettu typpilannoitus: vaikutukset kevätvehnän valkuaiseen ja $^{15}$N-merkityn lannoitetypen jakautumiseen maassa ja kasveissa

Tässä tutkimuksessa selvitettiin lannoitusajankohdan ja täydennyslannoitukseen käytetyn typpilannoitteen vaikutusta kevätvehnän satoon ja sadon laatuun, erityisesti valkuaispitoisuuteen ja valkuaisen leivontalaatuun, sekä $^{15}$N-merkityn lannoitetypen kulkeutumiseen eri kasvinosiin ja maahan.

Antamalla koko 140 kg/ha lannoitemäärä yhtenä annoksena kylvön yhteydessä saavutettiin kenttäkokeessa suurin sato. Antamalla 40 kg/ha osuus tästä määrästä kasvin pensomisvaiheessa tai tähkälletulovaiheessa sato aleni 3—5 %. Jyvän valkuaispitoisuus ja kostean sitkon määrä oli sitä korkeampi, mitä myöhäisempi oli lannoitus. Valkuaispitoisuus lisääntyi enimmillään 0.6 prosenttiyksikköä. Sakolukuun, hehtolitran painoon, tuhannen siemenen painoon tai leipätilavuuteen lannoituksen jakaminen ei vaikuttanut, mutta lakoutuminen väheni hiukan. Kasvunsäädekäsittely lisäsi satoa ja alensi valkuaispitoisuutta 0.3 prosenttiyksikköä. Kokeissa mukana olleet kaksi lajiketta, Heta ja Kadett, eivät poikenneet merkittävästi suhtautumisessaan jaettuun typpilannoitukseen.

Urearuiskutus tuotti täydennyslannoituksena alhaisemman valkuaispitoisuuden ja sitkon määrän kuin oulunsalpietari, kalkkisalpietari tai rakeinen urea. Täydennystyppilannoitteiden välillä ei ollut eroja vaikutuksessa satoon, leipätilavuuteen tai muihin tutkittuihin laatutekijöihin.

Astiakokeessa verrattiin seitsemää eri täydennystyppilannoituksen ajankohtaa kylvöstä kaksi viikkoa tähkälle tulon jälkeen. $^{15}$N-merkityn typen hyväksikäyttöaste oli korkein ylimmän lehden asteen lannoituksesta.

Kenttäkokeessa $^{15}$N-merkityn typen hyväksikäyttöaste oli korkein sateisena vuonna tähkälletulovaiheen lannoituksesta ja kuivana vuonna kylvön yhteydessä suoritetusta lannoituksesta. Kahtena muuna koevuotena lannoitusajankohta ei vaikuttanut hyväksikäyttöasteeseen. Kuivana kesänä lannoitetypen hyväksikäyttöaste oli 15—25 % ja kesinä, jolloin kosteutta oli riittävästi, 60—70 % parhaimmillaan. Urearuiskutuksena annetun typen hyväksikäyttöaste oli alhaisempi kuin nitraattina maan pintaan tai kylvölannoituksena annetun ammoniumnitraattitypen.

Lannoitusajankohta ei selvästi vaikuttanut $^{15}$N-merkityn epäorgaanisen typen määriin maassa 0—90 cm syvyydellä korjuuaikaan. Kasvustoruiskutuksena annettua urean typpeä oli epäorgaanisena typpenä maassa vähemmän, mutta orgaanisessa muodossa enemmän, kuin pintalannoituksena nitraattina tai kylvön yhteydessä ammoniumnitraattina annettua typpeä. Maan epäorgaanisesta typestä sadonkorjuuvaiheessa yli 80 % oli peräisin muista lähteistä kuin täydennyslannoituksista. Kuivan alkukesän jälkeen maassa oli sadonkorjuuvaiheessa runsaasti epäorgaanista typpeä.

Astiakokeessa jyvän proteiinien gliadiini-, gluteniini- ja jäännösproteiinifraktioiden määrä, mutta ei albumiinien + globuliinien määrä, lisääntyi sitä enemmän mitä myöhäisempi oli typpilannoitus. Kenttäkokeessa vastaavia lisäyksiä ei todettu. $^{15}$N-merkityn täydennyslannoitetypen osuudet vastasivat muista lähteistä peräisin olevan typen suhteellisia osuuksia proteiinifraktioissa.

Sääolot ovat syy vehnän alhaisiin valkuaispitoisuuksiin Suomessa joinakin vuosina. Ne myös aiheuttavat suurimman osan valkuaispitoisuuksien vuosittaisesta vaihtelusta. Tämä tutkimus ja suurin osa aikaisemmista tutkimuksista osoittavat, että jaetulla typpilannoituksella ei ole suuria mahdollisuuksia lisätä kevätvehnän valkuaispitoisuutta Suomessa. Valkuaispitoisuutta tulisi pyrkiä kohottamaan kasvinjalostuksen keinoin.

The effect of top dressing of nitrogen fertilizer on the yield (kg/ha) of Heta (1986 Luja) at Jokioinen and at Mietoinen in 1986—1989.

| | Jokioinen | | | | Mietoinen | | | | Mean |
|---|---|---|---|---|---|---|---|---|---|
| | -86 | -87 | -88 | -89 | -86 | -87 | -88 | -89 | |
| Unfertilized | — | — | 1130 | 1720 | — | — | 1570 | 1560 | — |
| 100 kg/ha N in spring | 1710 | 4190 | 1740 | 3770 | 4190 | 2500 | 2750 | 3780 | 3080 |
| 140 kg/ha N in spring | 1810 | 4130 | 1810 | 4150 | 4430 | 2930 | 2900 | 4050 | 3280 |
| 140 » in spring + CCC | 1820 | 4400 | 1960 | 4180 | 4340 | 3160 | 2990 | 4210 | 3380 |
| 100 » + 40 kg/ha N as CAN, tillering | 1820 | 3830 | 1910 | 3940 | 4000 | 2960 | 3140 | 3980 | 3200 |
| 100 » » ear emergence | 1750 | 4050 | 1800 | 3970 | 3950 | 2880 | 3120 | 3840 | 3170 |
| 100 » + 40 kg/ha N as CN, tillering | 1640 | 4050 | 1930 | 3950 | 4180 | 3040 | 3010 | 4220 | 3250 |
| 100 » » ear emergence | 1730 | 4230 | 1790 | 4080 | 3980 | 2800 | 2960 | 4080 | 3210 |
| 100 » + 40 kg/ha N as urea, granular, tillering | 1690 | 4230 | 2040 | 3910 | 4050 | 2780 | 2850 | 4120 | 3210 |
| 100 » » » » ear emergence | 1680 | 4040 | 1930 | 3850 | 3930 | 2820 | 2840 | 3940 | 3130 |
| 100 » + 40 kg/ha N as urea, foliar, tillering | 1820 | 3970 | 1930 | 4340 | 3840 | 2810 | 2590 | 4200 | 3190 |
| 100 » » » » ear emergence | 1870 | 4000 | 1960 | 4220 | 3960 | 2720 | 2680 | 4190 | 3200 |
| Fertilizers for top dressing | | | | | | | | | |
| CAN | 1790 | 3940 | 1850 | 3950 | 3970 | 2920 | 3130 | 3910 | 3180 |
| CN | 1680 | 4140 | 1860 | 4020 | 4080 | 2920 | 2990 | 4150 | 3230 |
| Urea, granular | 1690 | 4130 | 1990 | 3880 | 3990 | 2800 | 2850 | 4030 | 3170 |
| Urea, foliar | 1850 | 3980 | 1950 | 4280 | 3900 | 2770 | 2630 | 4200 | 3190 |
| Times of application of top dressing | | | | | | | | | |
| Tillering | 1740 | 4020 | 1950 | 4030 | 4020 | 2900 | 2900 | 4130 | 3210 |
| Ear emergence | 1760 | 4080 | 1870 | 4030 | 3950 | 2810 | 2900 | 4020 | 3180 |
| Statistical significance of differences | | | | | | | | | |
| All treatments except unfertilized | | | | | | | | | |
| Fertilizer | ns | ns | ns | ns | *** | ** | * | ** | ns |
| 140 kg/ha N in spring vs. top dressings | | | | | | | | | |
| Fertilizer | ns | ns | ns | ns | *** | ns | * | * | ns |
| Time of application | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| Fertilizer * time of application | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| Top dressings only | | | | | | | | | |
| Fertilizer | ns | ns | ns | ns | ns | ns | ** | * | ns |
| Time of application | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| Fertilizer * time of application | ns | ns | ns | ns | ns | ns | ns | ns | ns |

The effect of top dressing of nitrogen fertilizer on the yield (kg/ha) of Kadett at Jokioinen and at Mietoinen in 1986—1989.

| | Jokioinen | | | | Mietoinen | | | | Mean |
|---|---|---|---|---|---|---|---|---|---|
| | -86 | -87 | -88 | -89 | -86 | -87 | -88 | -89 | |
| Unfertilized | — | — | 1530 | 1590 | — | — | 1970 | 1720 | — |
| 100 kg/ha N in spring | 2480 | 2890 | 2470 | 4170 | 4270 | 2600 | 4060 | 4080 | 3380 |
| 140 kg/ha N in spring | 2840 | 3080 | 2700 | 4710 | 4790 | 2460 | 4460 | 4420 | 3680 |
| 140 » in spring + CCC | 2780 | 3120 | 2810 | 4580 | 4610 | 3200 | 4900 | 4360 | 3800 |
| 100 » + 40 kg/ha N as CAN, tillering | 2510 | 2820 | 2440 | 4130 | 4550 | 2790 | 4380 | 4240 | 3480 |
| 100 » » ear emergence | 2480 | 3030 | 2390 | 4150 | 4550 | 2860 | 4280 | 4080 | 3480 |
| 100 » + 40 kg/ha N as CN, tillering | 2070 | 3080 | 2730 | 3820 | 4490 | 2650 | 4670 | 4470 | 3500 |
| 100 » » ear emergence | 2160 | 3110 | 2540 | 3920 | 4310 | 2710 | 4400 | 4230 | 3420 |
| 100 » + 40 kg/ha N as urea, granular, tillering | 2490 | 3230 | 2460 | 4340 | 4500 | 2590 | 4330 | 3760 | 3460 |
| 100 » » » » ear emergence | 2440 | 3260 | 2370 | 4360 | 4380 | 2970 | 4270 | 3800 | 3480 |
| 100 » + 40 kg/ha N as urea, foliar, tillering | 2520 | 3100 | 2540 | 4140 | 4670 | 2700 | 4360 | 3970 | 3500 |
| 100 » » » » ear emergence | 2460 | 3310 | 2580 | 4120 | 4520 | 2920 | 4140 | 3910 | 3490 |
| Fertilizers for top dressing | | | | | | | | | |
| CAN | 2500 | 2920 | 2420 | 4140 | 4550 | 2820 | 4330 | 4160 | 3480 |
| CN | 2120 | 3090 | 2630 | 3870 | 4400 | 2680 | 4540 | 4350 | 3460 |
| Urea, granular | 2470 | 3240 | 2410 | 4350 | 4440 | 2780 | 4300 | 3780 | 3470 |
| Urea, foliar | 2490 | 3200 | 2560 | 4130 | 4590 | 2810 | 4250 | 3940 | 3500 |
| Times of application of top dressing | | | | | | | | | |
| Tillering | 2400 | 3060 | 2540 | 4110 | 4550 | 2680 | 4440 | 4110 | 3490 |
| Ear emergence | 2390 | 3180 | 2470 | 4140 | 4440 | 2870 | 4270 | 4010 | 3470 |
| Statistical significance of differences | | | | | | | | | |
| All treatments except unfertilized | | | | | | | | | |
| Fertilizer | * | ns | * | *** | * | ** | ** | *** | *** |
| 140 kg/ha N in spring vs. top dressings | | | | | | | | | |
| Fertilizer | ** | ns | ns | ** | ns | ns | ns | *** | ns |
| Time of application | ns | ns | ns | ns | ns | * | ns | ns | ns |
| Fertilizer * time of application | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| Top dressings only | | | | | | | | | |
| Fertilizer | * | ns | ns | * | ns | ns | ns | *** | ns |
| Time of application | ns | ns | ns | ns | ns | * | ns | ns | ns |
| Fertilizer * time of application | ns | ns | ns | ns | ns | ns | ns | ns | ns |

The effect of top dressing of nitrogen fertilizer on the protein content (%) of Heta (year 1986 Luja) at Jokioinen and at Mietoinen in 1986—1989.

| | Jokioinen | | | | Mietoinen | | | | Mean |
|---|---|---|---|---|---|---|---|---|---|
| | -86 | -87 | -88 | -89 | -86 | -87 | -88 | -89 | |
| Unfertilized | — | — | 17.7 | 16.5 | — | — | 12.7 | 11.7 | 14.7 |
| 100 kg/ha N in spring | 17.6 | 14.5 | 18.0 | 17.7 | 13.2 | 12.2 | 13.5 | 12.5 | 14.9 |
| 140 kg/ha N in spring | 18.2 | 14.5 | 18.7 | 18.5 | 13.9 | 12.7 | 14.9 | 14.7 | 15.8 |
| 140 » in spring + CCC | 17.9 | 14.6 | 18.0 | 18.1 | 14.1 | 12.2 | 14.7 | 14.3 | 15.5 |
| 100 » + 40 kg/ha N as CAN, tillering | 17.4 | 15.6 | 18.6 | 18.5 | 14.4 | 12.7 | 14.1 | 14.7 | 15.8 |
| 100 » » ear emergence | 18.0 | 15.1 | 18.6 | 17.4 | 14.3 | 13.4 | 15.5 | 15.7 | 16.0 |
| 100 » + 40 kg/ha N as CN, tillering | 18.0 | 15.2 | 18.2 | 18.8 | 14.9 | 13.1 | 15.8 | 14.5 | 16.1 |
| 100 » » ear emergence | 18.3 | 15.6 | 18.4 | 18.9 | 15.0 | 11.3 | 16.5 | 16.2 | 16.3 |
| 100 » + 40 kg/ha N as urea, granular, tillering | 18.0 | 15.0 | 17.8 | 18.5 | 14.4 | 12.7 | 15.1 | 14.2 | 15.7 |
| 100 » » » » ear emergence | 18.4 | 15.6 | 18.3 | 19.1 | 13.9 | 13.0 | 15.8 | 14.9 | 16.1 |
| 100 » + 40 kg/ha N as urea, foliar, tillering | 18.5 | 15.2 | 18.1 | 18.7 | 14.3 | 12.5 | 15.3 | 13.6 | 15.8 |
| 100 » » » » ear emergence | 18.0 | 14.4 | 18.4 | 18.9 | 13.7 | 12.4 | 15.0 | 13.9 | 15.6 |
| Fertilizers for top dressing | | | | | | | | | |
| CAN | 17.7 | 15.4 | 18.6 | 17.9 | 14.3 | 13.1 | 14.8 | 15.2 | 15.9 |
| CN | 18.2 | 15.4 | 18.3 | 18.8 | 15.0 | 12.2 | 16.2 | 15.4 | 16.2 |
| Urea, granular | 18.2 | 15.3 | 18.1 | 18.8 | 14.1 | 12.8 | 15.5 | 14.5 | 15.9 |
| Urea, foliar | 18.2 | 14.8 | 18.3 | 18.8 | 14.0 | 12.4 | 15.2 | 13.8 | 15.7 |
| Times of application of top dressing | | | | | | | | | |
| Tillering | 18.0 | 15.3 | 18.2 | 18.6 | 14.5 | 12.8 | 15.1 | 14.3 | 15.8 |
| Ear emergence | 18.2 | 15.2 | 18.4 | 18.6 | 14.2 | 12.5 | 15.7 | 15.2 | 16.0 |
| Statistical significance of differences | | | | | | | | | |
| All treatments except unfertilized | | | | | | | | | |
| Fertilizer | ns | ns | ns | ns | — | ** | ns | *** | *** |
| 140 kg/ha N in spring vs. top dressings | | | | | | | | | |
| Fertilizer | ns | ns | ns | ns | — | ** | ns | *** | ns |
| Time of application | ns | ns | ns | ns | — | ns | ns | *** | ns |
| Fertilizer * time of application | ns | ns | ns | ns | — | *** | ns | ** | ns |
| Top dressings only | | | | | | | | | |
| Fertilizer | ns | ns | ns | ns | — | ** | ns | *** | ns |
| Time of application | ns | ns | ns | ns | — | ns | ns | *** | ns |
| Fertilizer * time of application | ns | ns | ns | ns | — | *** | ns | ** | ns |

The effect of top dressing of nitrogen fertilizer on the protein content (%) of Kadett at Jokioinen and at Mietoinen in 1986—1989.

| | Jokioinen | | | | Mietoinen | | | | Mean |
|---|---|---|---|---|---|---|---|---|---|
| | -86 | -87 | -88 | -89 | -86 | -87 | -88 | -89 | |
| Unfertilized | — | — | 13.9 | 12.1 | — | — | 10.3 | 10.7 | 11.8 |
| 100 kg/ha N in spring | 15.8 | 10.8 | 15.5 | 13.1 | 12.6 | 10.5 | 11.3 | 10.6 | 12.5 |
| 140 kg/ha N in spring | 17.2 | 11.3 | 15.5 | 13.4 | 13.2 | 11.1 | 11.9 | 11.8 | 13.2 |
| 140 » in spring + CCC | 16.1 | 11.3 | 15.3 | 13.9 | 12.8 | 10.5 | 12.4 | 11.7 | 13.0 |
| 100 » + 40 kg/ha N as CAN, tillering | 17.2 | 11.8 | 15.6 | 13.8 | 13.1 | 11.1 | 13.8 | 11.7 | 13.5 |
| 100 » » ear emergence | 17.3 | 11.7 | 15.9 | 13.2 | 13.6 | 10.6 | 13.7 | 12.8 | 13.6 |
| 100 » + 40 kg/ha N as CN, tillering | 17.6 | 11.6 | 15.1 | 13.8 | 12.9 | 11.1 | 13.9 | 11.8 | 13.5 |
| 100 » » ear emergence | 17.7 | 11.9 | 16.2 | 14.0 | 13.9 | 10.9 | 14.0 | 12.9 | 14.0 |
| 100 » + 40 kg/ha N as urea, granular, tillering | 17.1 | 12.0 | 15.1 | 13.9 | 12.9 | 10.5 | 12.9 | 12.4 | 13.4 |
| 100 » » » » ear emergence | 16.9 | 12.1 | 15.5 | 14.3 | 13.5 | 10.7 | 12.4 | 13.0 | 13.5 |
| 100 » + 40 kg/ha N as urea, foliar, tillering | 17.4 | 11.4 | 15.3 | 13.0 | 13.0 | 10.7 | 11.7 | 11.6 | 13.0 |
| 100 » » » » ear emergence | 17.1 | 11.7 | 15.1 | 14.1 | 12.4 | 10.4 | 11.7 | 11.7 | 13.0 |
| Fertilizers for top dressing | | | | | | | | | |
| CAN | 17.2 | 11.7 | 15.7 | 13.5 | 13.3 | 10.8 | 13.7 | 12.2 | 13.6 |
| CN | 17.7 | 11.7 | 15.7 | 13.9 | 13.4 | 11.0 | 14.0 | 12.4 | 13.7 |
| Urea, granular | 16.7 | 12.0 | 15.3 | 14.1 | 13.2 | 10.6 | 12.7 | 12.7 | 13.4 |
| Urea, foliar | 17.2 | 11.6 | 15.2 | 13.6 | 12.7 | 10.6 | 11.7 | 11.7 | 13.0 |
| Times of application of top dressing | | | | | | | | | |
| Tillering | 17.3 | 11.7 | 15.3 | 13.6 | 13.0 | 10.8 | 13.1 | 11.9 | 13.3 |
| Ear emergence | 17.2 | 11.8 | 15.7 | 13.9 | 13.3 | 10.7 | 13.0 | 12.6 | 13.5 |
| Statistical significance of differences | | | | | | | | | |
| All treatments except unfertilized | | | | | | | | | |
| Fertilizer | * | *** | ns | ns | — | ns | ** | *** | *** |
| 140 kg/ha N in spring vs. top dressings | | | | | | | | | |
| Fertilizer | ns | ** | ns | ns | — | ns | ** | *** | *** |
| Time of application | ns | ns | * | ns | — | ns | ns | *** | * |
| Fertilizer * time of application | ns | ns | * | ns | — | ns | ns | ** | ns |
| Top dressings only | | | | | | | | | |
| Fertilizer | ns | * | ns | ns | — | ns | ** | *** | *** |
| Time of application | ns | ns | * | ns | — | ns | ns | *** | * |
| Fertilizer * time of application | ns | ns | * | ns | — | ns | ns | ** | ns |

The effect of time of application of top dressing of $^{15}N$-labelled nitrogen fertilizer on yield, nitrogen content, nitrogen yield and recovery of $^{15}N$-labelled nitrogen in different plant parts in the pot experiment. Nitrogen fertilization: basic 1000 mg/pot, top dressing 517 mg/pot. The results within the same column followed by the same letter do not differ statistically significantly according to Tukey's test (P = 0.05).

| Time of nitrogen application | Grain | Chaff | Straw highest internode | Straw 2nd highest internode | Straw 3—4th highest internodes | Roots | Plant total | Soil | Plant + soil |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Yield g DM/pot | | | | |
| No top dressing | $28.5^{b}$ | $8.1^{a}$ | $14.1^{c}$ | $12.0^{a}$ | $17.8^{a}$ | $7.0^{a}$ | $87.5^{b}$ | — | — |
| Sowing | $34.9^{a}$ | $9.5^{a}$ | $17.2^{a}$ | $13.7^{a}$ | $18.8^{a}$ | $5.3^{b}$ | $99.4^{a}$ | — | — |
| Tillering | $33.3^{ab}$ | $9.4^{a}$ | $17.1^{a}$ | $13.2^{a}$ | $17.9^{a}$ | $6.7^{ab}$ | $97.6^{ab}$ | — | — |
| Stem elongation | $31.5^{ab}$ | $9.3^{a}$ | $16.4^{ab}$ | $12.6^{a}$ | $18.4^{a}$ | $6.3^{ab}$ | $94.4^{ab}$ | — | — |
| 2-node stage | $33.1^{ab}$ | $9.4^{a}$ | $17.2^{a}$ | $13.2^{a}$ | $18.4^{a}$ | $5.4^{ab}$ | $96.7^{ab}$ | — | — |
| Flag leaf stage | $33.8^{ab}$ | $8.9^{a}$ | $14.9^{bc}$ | $12.5^{a}$ | $17.6^{a}$ | $5.7^{ab}$ | $93.3^{ab}$ | — | — |
| Ear emergence | $34.2^{ab}$ | $8.8^{a}$ | $15.2^{bc}$ | $12.4^{a}$ | $18.7^{a}$ | $5.9^{ab}$ | $95.2^{ab}$ | — | — |
| 2 weeks from ear emergence | $32.0^{ab}$ | $8.0^{a}$ | $14.2^{c}$ | $12.8^{a}$ | $16.1^{a}$ | $6.0^{ab}$ | $89.1^{b}$ | — | — |
| | | | | | Nitrogen content mg/g DM | | | | |
| No top dressing | $22.2^{c}$ | $4.3^{a}$ | $4.2^{b}$ | $2.9^{b}$ | $4.6^{de}$ | $7.8^{c}$ | — | $0.912^{ab}$ | — |
| Sowing | $26.0^{b}$ | $5.4^{a}$ | $5.4^{a}$ | $3.8^{a}$ | $6.8^{ab}$ | $10.3^{b}$ | — | $0.944^{a}$ | — |
| Tillering | $27.6^{ab}$ | $6.5^{a}$ | $5.9^{a}$ | $4.4^{a}$ | $7.4^{ab}$ | $11.4^{b}$ | — | $0.901^{b}$ | — |
| Stem elongation | $27.3^{ab}$ | $6.5^{a}$ | $5.9^{a}$ | $4.4^{a}$ | $8.1^{a}$ | $14.8^{a}$ | — | $0.926^{ab}$ | — |
| 2-node stage | $27.7^{ab}$ | $6.3^{a}$ | $5.8^{a}$ | $4.3^{a}$ | $6.5^{abc}$ | $15.7^{a}$ | — | $0.904^{b}$ | — |
| Flag leaf stage | $29.4^{ab}$ | $5.6^{a}$ | $5.9^{a}$ | $4.0^{a}$ | $6.3^{bcd}$ | $16.1^{a}$ | — | $0.923^{ab}$ | — |
| Ear emergence | $28.5^{ab}$ | $5.2^{a}$ | $5.3^{a}$ | $3.7^{a}$ | $5.1^{cde}$ | $16.4^{a}$ | — | $0.908^{b}$ | — |
| 2 weeks from ear emergence | $29.7^{a}$ | $5.0^{a}$ | $5.1^{ab}$ | $3.8^{a}$ | $4.5^{e}$ | $16.8^{a}$ | — | $0.933^{ab}$ | — |
| | | | | | Nitrogen yield mg/pot | | | | |
| No top dressing | $625^{b}$ | $35.1^{a}$ | $58.1^{d}$ | $34.5^{b}$ | $81.3^{cd}$ | $52.7^{d}$ | $887^{b}$ | $4886^{bc}$ | $5772^{c}$ |
| Sowing | $899^{a}$ | $50.5^{a}$ | $92.1^{ab}$ | $52.2^{a}$ | $128.6^{ab}$ | $53.4^{d}$ | $1276^{a}$ | $5074^{a}$ | $6350^{ab}$ |
| Tillering | $918^{a}$ | $60.8^{a}$ | $100.9^{a}$ | $58.5^{a}$ | $133.0^{ab}$ | $75.6^{c}$ | $1346^{a}$ | $4871^{c}$ | $6217^{b}$ |
| Stem elongation | $846^{a}$ | $61.2^{a}$ | $97.6^{ab}$ | $55.0^{a}$ | $149.6^{a}$ | $91.2^{ab}$ | $1310^{a}$ | $4979^{abc}$ | $6289^{ab}$ |
| 2-node stage | $913^{a}$ | $58.7^{a}$ | $99.7^{ab}$ | $56.6^{a}$ | $119.3^{abc}$ | $83.3^{bc}$ | $1331^{a}$ | $4924^{abc}$ | $6255^{ab}$ |
| Flag leaf stage | $989^{a}$ | $49.7^{a}$ | $87.3^{abc}$ | $49.2^{ab}$ | $110.1^{abcd}$ | $90.2^{ab}$ | $1376^{a}$ | $5021^{abc}$ | $6397^{a}$ |
| Ear emergence | $975^{a}$ | $45.9^{a}$ | $81.1^{bc}$ | $46.3^{ab}$ | $94.9^{cd}$ | $97.2^{a}$ | $1340^{a}$ | $4928^{abc}$ | $6268^{ab}$ |
| 2 weeks from ear emergence | $944^{a}$ | $39.2^{a}$ | $72.1^{cd}$ | $50.7^{a}$ | $73.2^{d}$ | $99.4^{a}$ | $1278^{a}$ | $5049^{ab}$ | $6327^{ab}$ |
| | | | | | % recovery of $^{15}N$-labelled fertilizer nitrogen | | | | |
| No top dressing | — | — | — | — | — | — | — | — | — |
| Sowing | $50.9^{c}$ | $2.7^{a}$ | $5.1^{bc}$ | $2.8^{b}$ | $7.4^{a}$ | $2.6^{f}$ | $71.6^{b}$ | $14.0^{a}$ | $85.6^{ab}$ |
| Tillering | $57.0^{bc}$ | $3.6^{a}$ | $6.0^{ab}$ | $3.5^{a}$ | $8.2^{a}$ | $3.6^{cd}$ | $81.7^{ab}$ | $9.6^{c}$ | $91.3^{ab}$ |
| Stem elongation | $54.8^{bc}$ | $3.8^{a}$ | $6.0^{ab}$ | $3.5^{a}$ | $8.1^{a}$ | $4.0^{cd}$ | $80.0^{ab}$ | $9.5^{c}$ | $89.5^{ab}$ |
| 2-node stage | $63.5^{ab}$ | $4.0^{a}$ | $6.8^{a}$ | $3.3^{ab}$ | $4.0^{cd}$ | $3.1^{e}$ | $84.6^{a}$ | $8.5^{c}$ | $93.1^{ab}$ |
| Flag leaf stage | $70.6^{a}$ | $3.8^{a}$ | $5.3^{b}$ | $2.0^{c}$ | $2.8^{bc}$ | $3.2^{de}$ | $87.7^{a}$ | $8.7^{c}$ | $96.5^{a}$ |
| Ear emergence | $65.0^{ab}$ | $2.7^{ab}$ | $4.0^{c}$ | $1.7^{c}$ | $2.4^{bc}$ | $4.0^{b}$ | $79.8^{ab}$ | $10.0^{bc}$ | $89.8^{ab}$ |
| 2 weeks from ear emergence | $61.2^{abc}$ | $1.0^{b}$ | $2.3^{d}$ | $1.4^{c}$ | $1.5^{c}$ | $4.6^{a}$ | $72.0^{b}$ | $11.6^{b}$ | $83.6^{b}$ |

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 311—319 (1991)
Seria AGROGEOLOGIA ET -CHIMICA N. 159 — Sarja MAA JA LANNOITUS n:o 159

# EFFECTS OF THE ADDITION OF SULPHATE AND PHOSPHATE ON THE LEACHING OF SELENITE AND SELENATE IN ACIDIC SOILS

TOIVO YLÄRANTA

YLÄRANTA, T. 1991. **Effects of the addition of sulphate and phosphate on the leaching of selenite and selenate in acidic soils.** Ann. Agric. Fenn. 30: 311—319. (Agric. Res. Centre of Finland, Inst. Crop and Soil Sci., SF-31600 Jokioinen, Finland.)

A laboratory experiment was done to study the effects of application of sulphate and phosphate on the leaching of selenium added to soil columns. 124 mg P or S was added to the leaching tubes, which were 320 ml in volume. Selenium, Se 100 µg/soil column, was added either as sodium selenite or sodium selenate to clay soil, sandy loam and Carex peat with naturally low selenium contents. Sulphur was applied in the form of calcium sulphate, phosphorus in the form of calcium dihydrogen phosphate.

Only slight amounts of selenite, 0.0—2.0 % of the selenium added, was leached through a 20 cm column from all soils when phosphate or sulphate had not been added. The addition of phosphate or sulphate increased the leaching of selenite slightly.

On average, 79—92 % of selenium added in the form of sodium selenite was found in the top 5 cm of soil to which it had originally been added. During the laboratory experiment lasting 2.5 months, de-ionized water corresponding to the column of 500 mm was added to the leaching tubes.

In the pure selenate treatment, the mean flow of selenium was 11.9 % through clay, 75.4 % through Carex peat and 70.9 % through sandy loam.

The addition of phosphate or sulphate increased clearly the leaching of selenate in all soils. The addition of sulphate enhanced selenate leaching more effectively than the addition of phosphate, but the difference between the phosphate and the sulphate treatments was statistically significant only for clay soil.

Index words: selenium leaching, selenite, selenate, sulphate and phosphate addition, acidic soils.

## INTRODUCTION

The chemical form of inorganic selenium in the soil depends largely on the pH and oxidation-reduction potential (Eh) of the soil. Three oxidation states of selenium are stable within the Eh range existing in the environment, +6 (selenate), +4 (selenite), and 0 (elemental selenium). Selenium is commonly present in oxidized soils in the +4 and +6 oxidation states.

Elemental selenium is oxidized to selenite slowly. In acidic soils saturated with water, elemental selenium may even be reduced to selenide. Many micro-organisms in soil are capable of reducing selenate and selenite to elemental selenium, which is visible under the microscope as red grains (BAUTISTA and ALEXANDER 1972).

The selenium sorbing mineral constituents of soils are Al and Fe oxides, clay minerals, and calcite (GOLDBERG and GLAUBIG 1988). As selenite binds strongly with the active iron oxides in the soil, with the clay fraction and with organic matter (GISSEL-NIELSEN 1976, HAMDY and GISSEL-NIELSEN 1976, JOHN et al. 1976, HAMDY and GISSEL-NIELSEN 1977), its leaching from agricultural soil is generally negligible. Leaching of selenium is increased by liming and reduced by adding organic matter to the soil (JONES and BELLING 1967, GISSEL-NIELSEN and HAMDY 1977).

Ions with a low affinity for a proton also have a low affinity for the metal ions forming part of the surface oxides in the soil (BARROW and BOWDEN 1987); hence, it is predicted that the binding constant for selenate ions in soil will be low (BARROW and WHELAN 1989).

In Danish soils, selenate is 10—20 times more soluble than selenite (CARY and GISSEL-NIELSEN 1973). Most selenates are more soluble in water than the corresponding sulphates. Neither does selenate form poorly soluble compounds with cations, such as $Ca^{2+}$, that normally occur in soil (REUTER 1975); hence selenate is far more easily leached from soil than selenite (GEERING et al. 1968, BROWN and CARTER 1969).

GISSEL-NIELSEN and HAMDY (1977) reported that liming with $CaCO_3$ increased the leaching of selenite from two Danish soils containing clay fractions of 4.1 % and 15.8 %.

The addition of selenate to the most common multinutrient fertilizers used in agriculture and horticulture was started in Finland in 1984. Selenium, especially in the form of selenate, has caused environmental problems in some regions of the world (e.g. OHLENDORF 1989). This kind of situation occurs primarily under arid or semi-arid conditions, not very easily in a humid region, as in Finland.

However, in order to evaluate the effects of selenium application on the environment, it is necessary to know the susceptibility of selenite and selenate to leaching from the soils and the factors affecting this. A leaching experiment conducted by YLÄRANTA (1982) showed that selenate can be leached at least from peat soils.

The aim of this laboratory experiment was to obtain information about the effects of phosphate and sulphate on the leaching of selenium, added as selenite or selenate to different acidic soils.

## MATERIAL AND METHODS

The soils used in the leaching experiment were Carex peat, sandy loam and clay. The clay content ($ø < 0.002$ mm) was 16 % for sandy loam soil and 49 % for clay soil.

The Carex peat had a degree of humification of $H_{9-10}$ on the von POST scale, and contained 27.2 % inorganic matter as determined by ignition at 500 °C overnight. The clay contained 3.5 % organic carbon, the sandy loam 3.8 %. The pH($CaCl_2$) of the clay and sandy loam was 4.8, that of the Carex peat being 4.0.

The physical and chemical properties of the soil samples have been described in detail in an earlier publication (YLÄRANTA 1990).

A total of 72 PVC tubes 30 cm tall with an internal diameter of 45 mm, were used in the leaching experiment. The tubes were charged with 323 g of a lightly moist clay (258 g of dry soil, $ø \leq 2$ mm), 360 g of sandy loam (346 g, $ø \leq 2$ mm) or 193 g of Carex peat (87 g, $ø \leq 2$ mm). The tubes and the way the tubes were filled with soil have been described in detail in an earlier publication (YLÄRANTA 1982).

There were four replicates, the experimental plan being as follows:

Selenite addition
Selenate addition
Selenite + phosphate
Selenate + phosphate
Selenite + sulphate
Selenate + sulphate

124 mg P or S was added to the tubes. Sulphur was applied in the form of calcium sulphate, phosphorus in the form of calcium dihydrogen phosphate. Thus, the addition of sulphate and phosphate per unit of soil volume was similar to that in the pot experiment entitled "Effects of the addition of sulphate and phosphate on the selenium content of Italian rye grass" (YLÄRANTA 1990).

The soil was watered with de-ionized water both by capillary action and by adding water to the top of the column. The clay tubes contained, on average, 58.0 % water, the sandy loam tubes 44.8 % and the Carex peat tubes 230 %. The columns were allowed to stand for four weeks, to equilibrate.

A hole 18 mm in diameter and 5 mm deep was made in the top of the soil column with a plastic rod. One milliliter of an aqueous solution containing 100 µg Se as sodium selenite or selenate labelled with 740 kBq of $^{75}Se$ (Amersham International plc, Buckinghamshire, England) was measured into each of the holes. After the solution had been absorbed, the soils were covered with 40 ml of quartz sand (ø 0.2—0.5 mm). The leaching tubes were allowed to hang from their stands in the laboratory, with 250 ml beakers placed beneath them.

The way water was added to the top of the columns and the analysis of $^{75}Se$ from water samples have been described in detail in an earlier publication (YLÄRANTA 1982). The addition of water to the tops of the tubes was repeated ten times during the 2.5 month experimental period. Each addition of water corresponded to a water column of 50 mm. The main part of this, 60—70 ml of the total of 80 ml, ran through the soil column. Totally, the following amounts of water (of the 500 mm added) penetrated through the soil columns during the experiment, in mm and on average:

| | Clay | Sandy loam | Carex peat |
|---|---|---|---|
| Selenite addition | 421 | 432 | 403 |
| Selenate addition | 426 | 423 | 392 |
| Selenite + phosphate | 404 | 411 | 422 |
| Selenate + phosphate | 403 | 442 | 404 |
| Selenite + sulphate | 399 | 433 | 409 |
| Selenate + sulphate | 421 | 431 | 397 |

When the measurements had been completed, the soil column was divided into eight 2.5 cm sections. The $^{75}Se$ activity was measured from 5 ml soil samples after mixing. The radioactivity of each quartz sand filter bed was also measured in the same way.

Finally, the pH($CaCl_2$) of the soil column was measured. A soil sample representing the whole column was obtained by mixing the 5 ml samples taken from each column section.

Statistical analysis of the results was carried out using the "ANOVA-1" software of the MSTAT-C Microcomputer Statistical Program (Michigan State University, MI, U.S.A.).

For comparison of means of the results obtained in the experiment, DUNCAN's (1955) test was applied at the 1 % level of significance.

## RESULTS

Only slight amounts of selenite, 0.0—2.0 % of the selenium added in the form of selenite, leached from all soils without the addition of phosphate or sulphate, as detected in the wa-

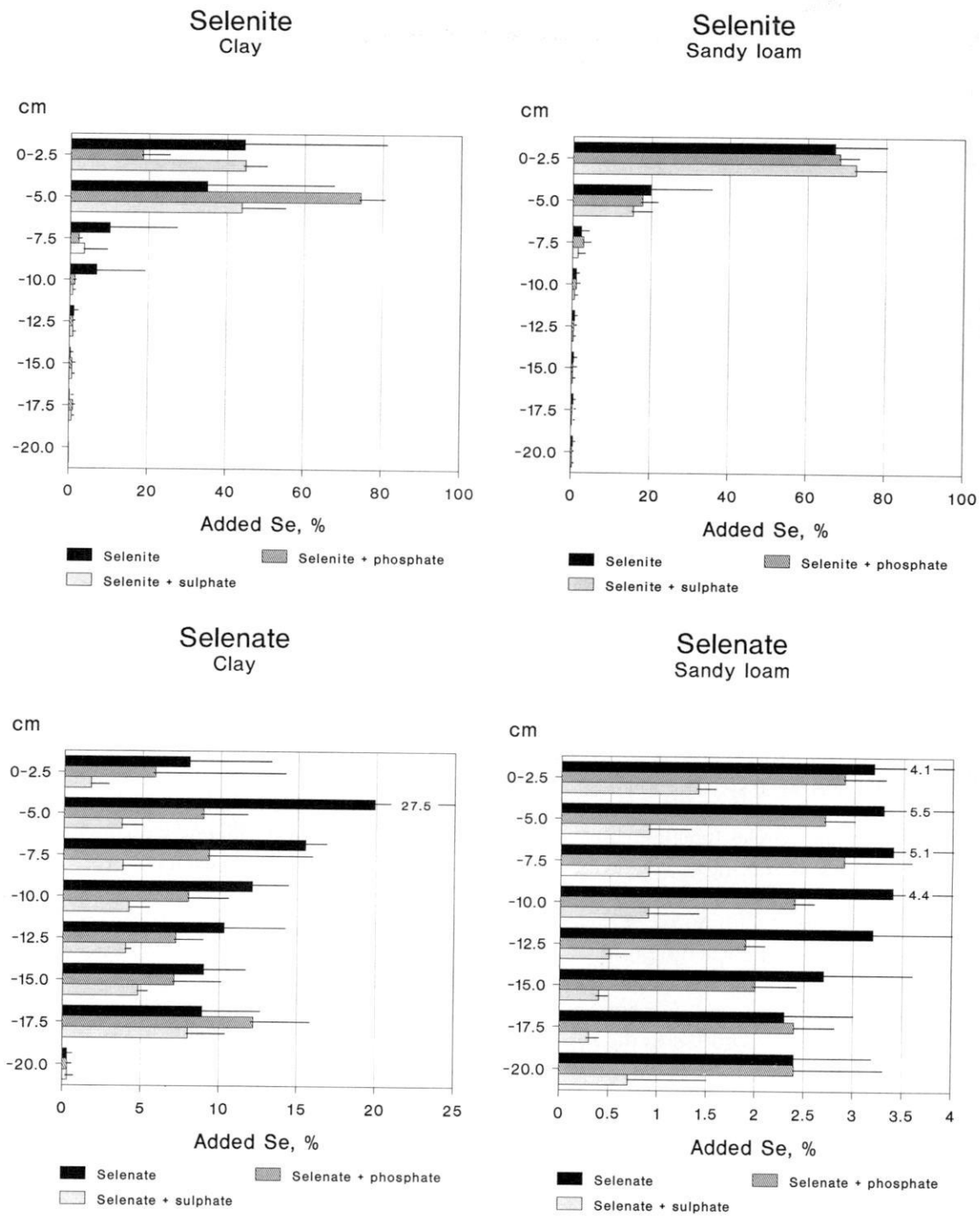


Fig. 1. The distribution of $^{75}$Se-labelled selenite and selenate in clay and sandy loam columns following leaching with 500 mm of water. The amount of radioactive selenium in the various soil layers is presented, together with 95 % confidence limits (the line describes the plus branch of the confidence limit), as a percentage of the selenium added to the column at the start of the experiment.

Table 1. Leaching of selenite and selenate added to the soil from a 20 cm soil column, expressed as a percentage of the selenium added. Figures given for each soil not marked with a common letter differ from each other at the 1 % level of significance (DUNCAN 1955). The mean pH($CaCl_2$) values at the end of the experiment were 4.7, 4.6 and 3.9 for clay, sandy loam and Carex peat, respectively.

| | Clay | Sandy loam | Carex peat |
|---|---|---|---|
| Selenite addition | 0.0[c] | 1.4[c] | 2.0[c] |
| Selenate addition | 11.9[c] | 70.9[b] | 75.4[b] |
| Selenite + phosphate | 0.5[c] | 3.9[c] | 1.6[c] |
| Selenate + phosphate | 37.2[b] | 79.1[ab] | 68.9[b] |
| Selenite + sulphate | 2.7[c] | 4.8[c] | 5.7[c] |
| Selenate + sulphate | 65.8[a] | 91.2[a] | 93.0[a] |

ter collected from the columns (Table 1).

The addition of phosphate or sulphate slightly increased the leaching of selenite from all soils, but the difference was not statistically significant. On average, 0.5—3.9 % of the selenium was leached through the soil column when phosphate was added. The highest figure was found for sandy loam, the lowest for clay.

The addition of sulphate enhanced selenite leaching slightly more effectively than did the addition of phosphate. The mean leaching of selenium varied in this treatment from 2.7 % to 5.7 %. The highest amount was leached from Carex peat.

Most of the selenium was passed through the "phosphate" and "sulphate" columns when 150—250 mm of water had been added.

In the selenite treatments, selenium moved slightly downward in the soil columns (Figs. 1 and 2). Still, on average, 79—92 % of the selenium added in the form of sodium selenite was analyzed in the top 5 cm of soil to which it had originally been added.

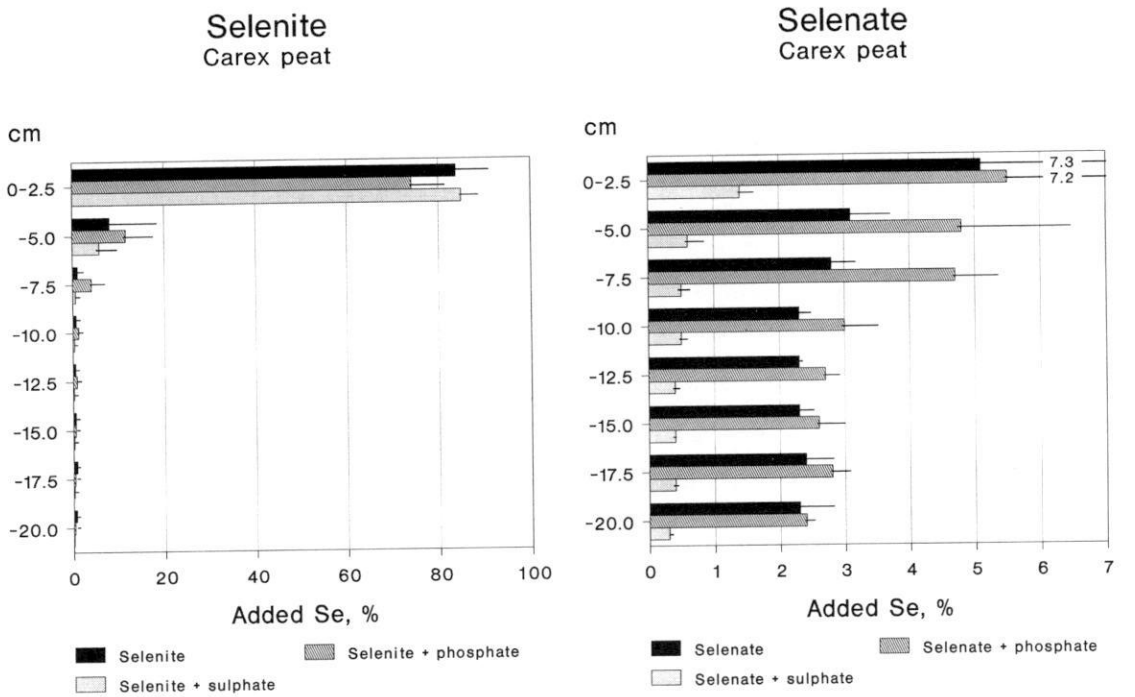


Fig. 2. The distribution of $^{75}Se$-labelled selenite and selenate in Carex peat columns following leaching with 500 mm of water. The amount of radioactive selenium in the various soil layers is presented, together with 95 % confidence limits (the line describes the plus branch of the confidence limit), as a percentage of the selenium added to the column at the start of the experiment.

In the pure selenate treatment, the flow of selenium was 11.9 % through clay, 75.4 % through Carex peat and 70.9 % through sandy loam (Table 1). On average, 6 % of the selenium was leached through the clay columns when 250 mm of water had been added. The respective figures were 66 % for sandy loam and 75 % for Carex peat.

The leaching of selenate from clay did not differ statistically significantly from that of selenite.

The addition of phosphate increased the leaching of selenate from clay and sandy loam. The flow of selenate through the sandy loam was highest, 79.1 %, and lowest, 37.2 %, through clay. The respective flow through the Carex peat was 68.9 %, a value slightly less than that without the addition of phosphate. Compared to the pure selenate treatment, the addition of phosphate increased the leaching of selenium statistically significantly only from clay.

The addition of sulphate enhanced the leaching of selenate more effectively than the phosphate addition for all soils, but the difference, as compared to the findings for phosphate treatment, was statistically significant only for clay and Carex peat. The highest leaching of selenate, 93.0 %, on average, was measured from Carex peat; it was 91.2 % from sandy loam and 65.8 % from clay.

In the sulphate treatment, the main part of the selenate leached was measured after the addition of 250 mm of water; the mean figures were 75 % for clay, 95 % for sandy loam and 99 % for Carex peat.

The selenate moved downward in each treatment in all soils (Figs. 1 and 2). Even in clay soil, selenate was moving downward in such a way that further addition of water might have leached the main part of selenate added through the column.

The quartz sand filter beds contained no notable amounts of $^{75}Se$.

The mean pH($CaCl_2$) values of the soils at the end of the experiment were $4.65 \pm 0.07$, $4.64 \pm 0.12$ and $3.85 \pm 0.12$ for clay, sandy loam and Carex peat, respectively, all at the 99 % confidence level. During the experiment, the pH($CaCl_2$) values in each soil decreased from the initial figures by 0.15 pH($CaCl_2$) units, on average.

## DISCUSSION

The leaching of selenite from all the acidic soils studied was slight. The leaching of selenite from soils still depends to some extent on the pH of the soil. Selenite sorption on soil is highest at low pH values and decreases at pH values higher than 7 (GOLDBERG and GLAUBIG 1988). Also NEAL et al. (1987 a) reported that selenite adsorption by alluvial soils, at environmentally relevant initial selenite concentrations of 2 to 8 mmol $m^{-3}$, decreases uniformly with increasing pH in the pH range of 4 to 9.

On the other hand, AHLRICHS and HOSSNER (1987) measured the elution and sorption characteristics of selenate and selenite in column studies. A composite of sandy loam textured stripmine overburden was adjusted to pH 2, 3, 5, 7, and 9 and packed into glass columns. Selenium, as the sodium salt of selenate or selenite, was added to the surface. Individual columns were leached with 1.5, 10, or 50 pore volumes of 0.01 M $CaCl_2$. Selenite was completely sorbed in the top 1 cm of the leaching columns at all pH values. Extensive leaching (50 pore volumes of 0.01 M $CaCl_2$) resulted in slight movement of selenite, to a maximum depth of 1.4 cm. Selenate was mobile at all pH

values, and was completely leached from columns with <3 pore volumes of solution.

The addition of sulphate increased the leaching of selenite only slightly. This result is not unexpected. In the study conducted by NEAL et al. (1987 b), sulphate had no effect on $SeO_3^{2-}$ adsorption at a $SO_4^{2-}$ concentration of 16 mol $m^{-3}$ in 50 mol $m^{-3}$ NaCl.

Selenite and o-phosphate are adsorbed in the soil by a similar mechanism, viz. ligand exchange (NEAL et al. 1987 b). Thus, theoretically, phosphate exchanges readily with specifically absorbed selenite (RĀJAN and WATKINSON 1976). An initial concentration of phosphate (2 µmol $kg^{-2}$ o-phosphate) comparable to that of selenite resulted in a decrease of selenite adsorbed on two alluvial soils from the San Joaquin Valley, California, U.S.A., the fall being approximately half (NEAL et al. 1987 b). In the present study the effect of phosphate addition on the selenite leaching was still small, even smaller than the effect of sulphate addition.

In the earlier leaching study conducted by YLÄRANTA (1982), the flow of selenium, originally added as selenate, was remarkably greater through the 20 cm clay and sandy loam columns than through mineral soils. Selenate passed through all soils very effectively even without the addition of phosphate or sulphate.

YLÄRANTA (1982) reported that less than 0.2 % of the selenium added in the form of sodium selenate (Se 100 µg/320 ml soil) was leached through the columns of clay soil or fine sandy soil during a two-month laboratory experiment.

The particle size distribution of the sandy soil used in this study and that in the YLÄRANTA's (1982) study were almost equal. The organic matter content of the sandy loam in this study was 3.8 % and that of the fine sandy soil used by YLÄRANTA (1982) 2.2 %.

Thus, the reason for the greater leaching of selenium measured in this study was not caused by differences in the main soil composition. The tubes were the same in both studies. Also the filling of the tubes with soils and the experimental conditions did not differ very much from each other.

The clay soil in YLÄRANTA's (1982) study contained more clay (ø < 0.002 mm, 62 %) than the clay soil in this study (49 %). Therefore, at least to some extent, differences in the particle size distributions in clay soils may explain the lesser leaching of selenium in YLÄRANTA's (1982) study than that measured in this study.

It is to some extent uncertain whether I really have measured pure selenite or selenate leaching. I did not check the chemical purity of the selenium compounds added to the top of soil columns and which flowed through the soils. AHLRICHS and HOSSNER (1987) reported that $Na_2{}^{75}SeO_3$ may contain significant levels of $Na_2{}^{75}SeO_4$. They stress that: "The unacknowledged occurrence of $Na_2{}^{75}SeO_4$ in the $Na_2{}^{75}SeO_3$ and vice versa should be addressed by anyone attempting experiments using radioactive Se".

GOLDBERG and GLAUBIG (1988) confirmed that retention of selenate in different types of soil is week and not very closely dependent on soil pH.

The anions $SeO_4^{2-}$ and, to some extent, $SO_4^{2-}$ are considered to be adsorbed mainly as diffuse-ion swarm and outer-sphere complex species (SPOSITIO 1989, p. 157—158). Sulphate is chemically related to selenate (BARROW and WHELAN 1989). Selenate has been found to behave in a manner similar to sulphate in four alluvial soils (NEAL and SPOSITIO 1989).

Thus, sulphate addition may enhance the leaching of selenate through soil. In the leaching experiments carried out by BROWN and CARTER (1969), sulphate increased the leaching of selenium added to the alkaline silt loam as barium selenate.

The selenate was very soluble, without addition of phosphate or sulphate, in sandy loam and peat; this at least partly explains the reasonably slight effects of these anions on the leaching of selenate from these soils.

It is somewhat surprising that the effect of sulphate on the leaching of selenite and selenate was more powerful in all soils than the addition of phosphate. One explanation may be the changes in ionic strength caused by the addition of sulphate. The addition of sulphate to the same soils as tested here, in an amount comparable to the addition in this study, caused a notable increase in the electrical conductivity of soils in the pot experiment conducted by YLÄRANTA (1990).

It is not known, how long selenate added to soil remains in selenate form, but it obviously persists as selenate for at least some months (YLÄRANTA 1983). It is open to question whether the selenate really was in the form of selenate or not when YLÄRANTA (1982) measured very limited selenate leaching through the soil columns as compared to the results of this study.

The addition of water to the leaching tubes and the flow of water through the soil columns was very high compared to the actual situation in the field. In Finland, the precipitation is not usually so high during the growing season that the penetration of leaching water in amounts comparable to this study would be possible. In the autumn, however, when plants no longer take water and the evaporation is also very limited, the water flow may run down through the soil profile. If the soil then contains excess soluble selenate selenium, selenium may actually be leached.

Therefore, the high leaching of added selenate from different soils shows that the retention and leaching of selenate must be studied in greater detail in natural field conditions. The possible reduction rate of selenate in our soils must be known more thoroughly in order to evaluate the fate of selenate applied through fertilizers.

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*Manuscript received May 1990*

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## SELOSTUS

# Fosfaatti- ja sulfaattilisäyksen vaikutus seleniitin ja selenaatin huuhtoutumiseen eri maissa

TOIVO YLÄRANTA

Maatalouden tutkimuskeskus

Seleeniä lisätään Suomessa lannoitteisiin selenaattimuodossa. Selenaatti on maassa hyvin liukoinen ja se on siksi ympäristöongelma eräissä maapallon osissa. Myös Suomessa on esiintynyt epäilyjä siitä, että selenaattilannoitus on uhka ympäristölle. Selenaatti pyrkii pelkistymään alemmille hapetusluvuille, kuten seleniitiksi, happamissa ja pelkistävissä maaperäoloissamme. Seleniitti pidättyy lujasti maahan, eikä ole yhtä altis huuhtoutumiselle kuin selenaatti. Selenaatin pelkistymisnopeutta viljelymaissamme ei tiedetä. Se ei myöskään ole helposti mitattavissa. Sen vuoksi on tärkeätä tietää, miten helposti selenaatti- ja seleniittimuotoinen seleeni huuhtoutuu eri maissa ja mitkä tekijät vaikuttavat seleenin huuhtoutumiseen.

Laboratoriossa suoritetussa huuhtoutumiskokeessa selvitettiin maahan seleniittinä ja selenaattina lisätyn seleenin (Se 100 µg/320 ml maata) huuhtoutumista 20 cm:n korkuisten savi-, hieta- ja saraturvepylväiden lävitse. Kahden ja puolen kuukauden aikana lisättiin huuhtoutumisputkiin 500 mm:n vesipatsasta vastaava vesimäärä kymmenessä erässä. Valtaosa tästä vedestä valui maapylväiden lävitse.

Seleniittinä lisätyn seleenin huuhtoutuminen maapylväiden lävitse oli vähäistä kaikissa maalajeissa, keskimäärin vain 0—2 %. Fosfaatin ja sulfaatin lisääminen maaputkiin tehosti lievästi seleniitin huuhtoutumista.

Keskimäärin 79—92 % seleniittinä lisätystä seleenistä löytyi kokeen loputtua 5 cm:n matkalta maapylvään siitä osasta, johon se kokeen alussa lisättiin.

Selenaattina lisätty seleeni huuhtoutui tehokkaasti maapylväiden lävitse. Valumavesistä mitattiin savimaassa keskimäärin 11.9 %, turvemaassa 75.4 % ja hietamaassa 70.9 % putkiin alunperin lisätystä selenaatista.

Fosfaatin ja sulfaatin lisääminen maapylväisiin tehosti selenaatin huuhtoutumista. Sulfaatin vaikutus oli kuitenkin suurempi kuin fosfaatin.

Kokeessa valutettiin lyhyessä ajassa maapylväiden lävitse suuri vesimäärä. Luonnossa vastaava tilanne ei ole kovin todennäköinen. Niinpä tuloksia ei voida suoraan soveltaa luonnonoloihin. Selenaatin huuhtoutuminen oli joka tapauksessa yllättävän runsasta. Onkin ehdottomasti pyrittävä käytännön oloissa selvittämään selenaatin huuhtoutumistaipumus. Samalla olisi pyrittävä selvittämään se, miten nopeasti selenaattina maahan lisätty seleeni pelkistyy oloissamme selenaattia vähemmän liukoisiin ja ympäristön kannalta riskittömämpiin seleenin muotoihin.

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 321—329 (1991)

Seria AGROGEOLOGIA ET -CHIMICA N. 160 — Sarja MAA JA LANNOITUS n:o 160

# CHEMICAL PROPERTIES OF AIR-DRIED SAMPLES FROM AN UNLIMED AND LIMED ACID SULPHATE SOIL PROFILE AND LEACHING OF ELEMENTS FROM THE PROFILES

RAIMO ERVIÖ

ERVIÖ, R. 1991. **Chemical properties of air-dried samples from an unlimed and limed acid sulphate soil profile and leaching of elements from the profiles.** Ann. Agric. Fenn. 30: 321—329. (Agric. Res. Centre of Finland, Inst. Crop and Soil Sci., SF-31600 Jokioinen, Finland.)

Leaching of acid sulphate soil limed and unlimed profiles (1 m) in laboratory condition with deionised water (equal to rainfall of 140 mm) 15 years after liming (32 tonnes $ha^{-1}$ limestone powder) reduced the electric conductivity and the extractable $SO_4$, Mg and Mn concentrations throughout the length of the unlimed profile as compared to the original values. The $SO_4$, Mg and Mn concentrations decreased in the deep layers of the limed profile as well, and the iron content increased in the uppermost layer.

Ca, Mg, Na, Al, Mn and $SO_4$-S concentrated in the uppermost layer of the unlimed soil profile as a consequence of evaporation flow of sulfate water underneath. In the surface layer of the limed profile, only Ca, Mg, Na and Mn concentrated to some extent, but no Al and $SO_4$, at all. No concentration of potassium or iron was observed. The electric conductivity of the upper most layer (0—3 cm) of the unlimed profile increased from five to 46, that of the limed profile to 17.

In the effluent water of unlimed soil, the $SO_4$ concentration remained unchanged (2 000 mg $l^{-1}$) throughout leaching (30 weeks); sulphur was leached the most from the limed soil. With a water quantity corresponding to a rainfall of 140 mm, 107 mg of $SO_4$-S was leached from unlimed soil per litre of soil. The leachates of iron and aluminium were higher in limed soil than in unlimed soil with all treatments, and the concentrations of the effluents were highest at the beginning of the trial.

Index words: acid sulphate soil, leaching of soil, $SO_4$-sulphur, aluminium, calcium, iron, magnesium, manganese, potassium, electric conductivity.

## INTRODUCTION

Areas of acid sulphate soils in Finland have been surveyed on various occasions. Most of these areas are located in the coastal regions of the Bothnic Gulf (PUROKOSKI 1959, ERVIÖ 1975). These soils have been sedimented during and after the ancient Baltic Basin Litorina Phase. They have been included in the international classification as "actual acid sulphate soils" (BRINKMAN and PONS 1973).

In addition to their high sulphur content, sulphate soils are characterised by a very low pH value in the oxidated state, by high electric conductivity, and by high iron and aluminium contents (PUROKOSKI 1958, KEVIE 1973).

When soils is taken for cultivation, the salt content of sulphate soils must be reduced. This is done by means of natural leaching accomplished by rainfall, or by liming; the latter also reduces the acidity. Leaching of iron and aluminium sulphate, on the other hand, cause acidification of the water of rivers and other watercourses, which may lead to the death of fish in the river and in the sea near the river mouth. Concrete drain pipes which are dug into salt-rich soil do not last; they are damaged when sulphate reacts with the calcium content of the concrete (HYYPPÄ 1977).

Even in the climatic conditions of Finland, during dry periods, salts have been shown to rise with capillary water to the soil surface, where crystallization of the salts has formed a light slag which is called alum (FROSTERUS 1914, AARNIO 1924, KIVINEN 1944).

In the present study, experimental transport of salts was caused in acid sulphate soil, upwards by evaporation and capillary force and downwards by leaching with a small quantity of water. By determining to what extent and how rapidly sulphate and some metals are transported in soil it is possible to reduce more effectively their detrimental effect to cultivation and watercourses.

## MATERIAL AND METHODS

The experimental area of acid sulphate soil was near the town of Vaasa; it had been dammed from the Bothnic Gulf in 1956. In 1971, soil profiles were taken from an unlimed plot of cultivated soil and from a plot of cultivated soil limed 15 years earlier. At that time 16 tn $ha^{-1}$ lime was applied, and four years later another 16 tn was applied. Soil columns were obtained by pressing plastic cylinders into the soil with a shovel loader of a tractor. The cylinders were 1 m high and 0.15 m in diameter; thus the volume of the soil column was 17.67 $dm^3$. When the soil columns were taken in early May, their moisture was close to the field capacity moisture.

The particle-size distribution of the profile, representing gyttja clay, was as follows: clay fraction (< 0.002 mm) 32—37 %, silt fraction (0.02—0.002 mm) 36—42 % and fine sand fraction (0.2—0.02 mm) 23—32 %. In the 0—0.2 m layer the organic matter content was 3.2—4.0 % and the bulk density 0.90, in the 0.2—1.0 m layer 1.7—2.1 % and 0.95, respectively.

The unlimed and limed soils were significantly different only in the surface layer of the soil columns, where they differed with respect to pH, electric conductivity, calcium, magnesium and $SO_4$-sulphur (Table 1).

### Analyses

The soil samples were taken from the soil column, at distances of fixed centimeters depth, upon termination of the trial. The soil samples were dried at 32—35 °C and ground to pass a 2-mm sieve. The concentrations are expressed per unit of volume of air-dried and ground soil. The soil pH and electric conductivity were measured from a soil-water suspension of the air-dried sample (volume ratio 1 : 2.5). The electric conductivity value given is for specific conductivity $10 \times$ mS $cm^{-1}$. Sulphate sulphur, calcium, potassium, magnesium, iron, aluminium and manganese were determined by atomic absorption spectrometry from the acid (pH 4.65) ammonium acetate extract of soil (1 : 10 = v : v), (VUORINEN and MÄKITIE 1955).

### Trial arrangements

The soil column cylinders were kept at room temperature for 30 weeks. The treatments were: 1) a soil column with deionised water leached downwards and 2) a soil column which was kept in a vessel filled with drainage water so that the evaporation occurring from the surface caused an upward capillary water flow. Leaching water, a total of 2.5 litres, was added during the trial at least 13 times. It equals a rainfall of 140 mm, and is approximately a quarter of the annual rainfall. The water used for capillary water rise treatment was taken from the drying drain of the experimental area, i.e. ground water deposited in the ditches. The pH of the water was 3.4 and the other concentrations were calcium 81, potassium 10, magnesium 92, manganese 10, iron 0.8, aluminium 64 and $SO_4$-S 360 mg $l^{-1}$. Both samples consisted of unlimed and limed soil. Samples from percolated water were taken four times. The percolation times were 64, 47, 50 and 48 days.

## RESULTS

The pH measured from a dried sample of limed soil was initially slightly higher than of unlimed soil (Fig. 1) only in the uppermost layer of the profile (0.4 m). During the trial, the pH rose to some extent in the whole unlimed leached profile and also in the lower part, 0.4—1.0 m, of the profile of limed soil. The pH values of impregnated soil tended to decrease towards the upper part of the profile (0—0.4 m) but to rise towards the bottom of the profile as in leached soil. The effect of leaching with deionised water could be seen in the uppermost layer of unlimed soil as a slightly elevated pH.

Leaching of soil reduced the initially relatively high electric conductivity of unlimed soil throughout the profile (Fig. 1). Reduction of

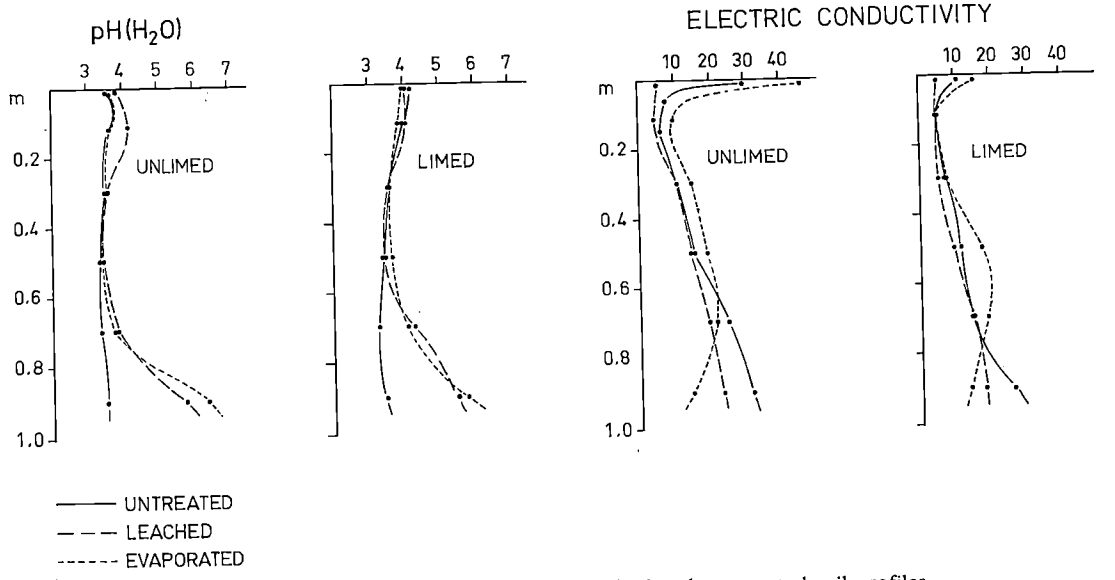


Fig. 1. The pH and electric conductivity in the untreated, leached and evaporated soil profiles.

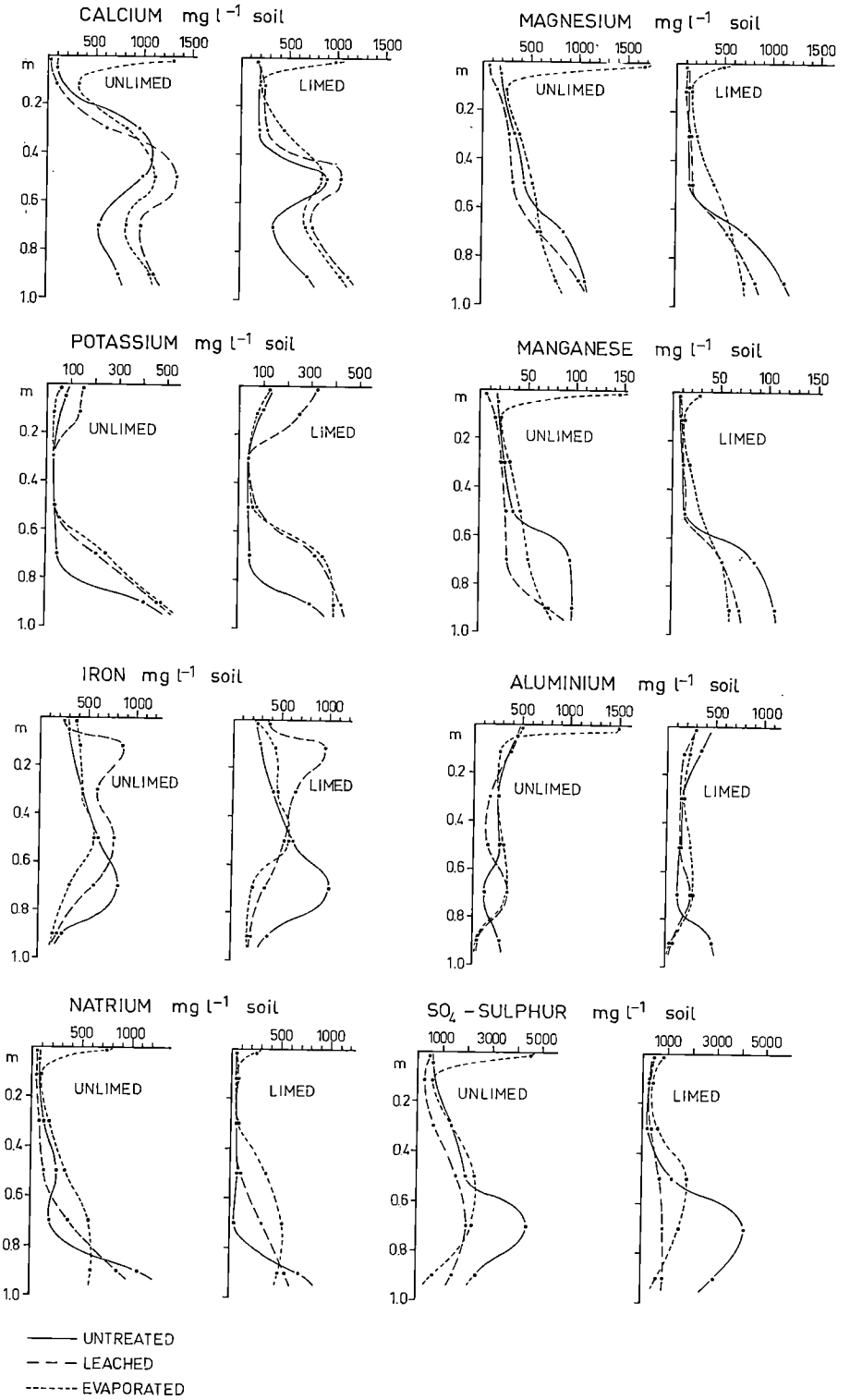


Fig. 2. Contents of the elements in soil profiles of the untreated, leached and evaporated treatments.

electric conductivity is naturally a result of salts being leached away from the soil profile. Inversely, the salts in the second treatment were transported by capillary upwards and were chrystallized as a result of water evaporating towards the soil surface, resulting in a strong elevation of electric conductivity. This occurred to a lesser extent also as a result of normal drying in the untreated soil profile.

Also in the limed soil, the change in calcium concentration mg $l^{-1}$ was relatively small (Fig. 2). Leaching further decreased the Ca concentration in the upper part of the unlimed soil profile, but not that in the limed soil. The calcium concentration increased in the middle and lower parts of the profile, whereas calcium was transported downwards as a result of leaching. Calcium was clearly concentrated to the surface in soils with an upward water flow. In these, the Ca concentration was 1 300 mg $l^{-1}$ soil in unlimed soil and 975 mg $l^{-1}$ soil in limed soil, whereas in leached soils it was only 25 and 175 mg $l^{-1}$, respectively.

**Magnesium** was leached downwards throughout the soil profile, and it was transported from the lower part of the impregnated soil column to the upper part of the column, especially to the uppermost layer of the soil (Fig. 2). In the surface of the unlimed soil, the magnesium content was 1 670 per mg $l^{-1}$ soil, whereas the baseline value for the 0.1 m layer was only 185 mg $l^{-1}$.

As a result of leaching, the concentration of extractable **potassium** seemed to double in the uppermost layer (0.2 m) of the unlimed and the limed soil (Fig. 2). Unlike calcium and magnesium, the water flow did not transport potassium to the soil surface. Its concentrations remained almost at the initial levels in the 0.2—0.4 m and 0.4—0.6 m layers with both treatments and in both soils. In the 0.6—0.8 m layer, on the other hand, the K values were almost fivefold and in limed soils almost fourfold the baseline values.

**Sodium** unlike potassium, increased in the uppermost layer of the limed and especially the unlimed impregnated soil (Fig. 2). In both impregnated soils, also the Na values of the 0.6—0.8 m layer were clearly increased as compared to the baseline values. Leaching had to some extend decreased the sodium concentration in the upper part (0—0.6 m) of the unlimed profile, and increased it in the 0.6—0.8 m layer both in the unlimed and in the limed profile.

**Manganese** seemed to be leached away from the lower part of the profile where it was initially recovered abundantly, and to be transported in the impregnation treatment also towards the 0.2—0.6 m layer and to the soil surface, especially in the unlimed soil profile (Fig. 2).

Leaching of the soil increased the content of extractable **iron** in the 0.03—0.20 m and 0.2—0.4 m layers, but decreased it especially in the 0.6—0.8 m layer (Fig. 2). The highest iron concentration of the profile was observed in the latter layer, which represented approximately the lower limit of the oxidated horizon and where the soil pH, 3.3, was lowest. In the impregnation treatment the iron content increased also in the 0.03—0.20 m layer, but it was not accumulated at the very surface of the soil.

In leached soil, **aluminium** seemed to be transported from the part of the profile above 0.6 m to the 0.6—0.8 m layer (Fig. 2). In the impregnation treatment aluminium was very highly concentrated in the uppermost layer of the unlimed soil, but not in the uppermost layer of the limed soil. In the unlimed soil surface as much as 1490 mg Al $l^{-1}$ was recovered, whereas in the original soil there was only 500 mg.

**Sulphate sulphur** seemed to be leached throughout the profile of the untreated soil and from the lower part of limed soil where $SO_4$ sulphur occurred most abundantly (Fig. 2). In the impregnated soils sulphate sulphur was also decreased in the lower parts of the profiles, and was to some extent transported to the middle parts, in the unlimed soil abundantly also to the

uppermost layer. Its $SO_4$ sulphur concentration was 4 500 mg $l^{-1}$ soil, whereas in the original and leached soil it was only approx. 500 mg.

## Effluent water concentrations

The **pH value** of the water percolated through the unlimed soil was 3.9 in the beginning of the treatment and 4.7—4.8 towards the end (Table 2). The pH of the effluent water of limed soil was below 3 throughout the trial.

The **electric conductivity** measured in the effluent remained at 100—110 in the unlimed soil throughout the trial, and in the limed soil it decreased from 90 to 70.

The **sulphate sulphur** concentration in the subsequent extractings remained almost unchanged occasionally, especially in the limed soil was about 50 % higher than in the unlimed soil.

**Iron** was extracted clearly more in the beginning of the trial than in the middle and at the end of the trial, both from the unlimed and from the limed soil. The total amount of iron 8.5 mg $l^{-1}$ soil extracted from the limed soil was of a far different magnitude than the 0.12 mg $l^{-1}$ soil extracted from the unlimed soil. As with iron, clearly more **aluminium**, 10.6 mg $l^{-1}$, was extracted from limed soil than from unlimed soil, 0.3 mg $l^{-1}$. In the concentrations of aluminium extracted from unlimed soil, a clear decrease (8 mg $l^{-1}$), to the level 1—2 mg $l^{-1}$, was seen after second water sampling.

**Manganese** was extracted in the beginning of

Table 1. Some exceptional chemical properties in unlimed and limed profiles of the original soil.

| Depth m | pH($H_2O$) | | Electric conductivity 10 × mS/cm | | Acid AAc (pH 4.65)-extractable | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Calcium | | Magnesium | | $SO_4$-S | |
| | unlimed 1. | limed 2. | 1. | 2. | 1. | 2. | 1. | 2. | 1. | 2 |
| 0.2 | 3.90 | 4.15 | 8.2 | 4.8 | 100 | 200 | 185 | 131 | 620 | 250 |
| 0.2—0.4 | 3.55 | 3.80 | 13.5 | 3.8 | 950 | 200 | 315 | 130 | 1400 | 220 |
| 0.4—0.6 | 3.30 | 3.35 | 18.1 | 10.5 | 1000 | 900 | 438 | 152 | 1950 | 1200 |

Table 2. Contents of the seep waters gathered in the rinsing time.

| Leaching rounds | | Sampling ml | pH | Conductivity | mg/litre solution | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Fe | Al | Mn | $SO_4$-S | Ca | K | Mn |
| Unlimed | 1. | 220 | 3.9 | 111 | 7.1 | 7.8 | 22 | 1975 | not analysed | | |
| | 2. | 260 | 4.2 | 98 | 1.1 | 7.9 | 20 | 1975 | » | | |
| | 3. | 260 | 4.8 | 110 | 0.5 | 2.4 | 27 | 1875 | 340 | 180 | 1075 |
| | 4. | 230 | 4.7 | 110 | 0.3 | 1.1 | 38 | 1975 | 336 | 185 | 1215 |
| Limed | 1. | 400 | 2.9 | 91 | 126 | 19.7 | 38 | 1600 | not analysed | | |
| | 2. | 350 | 2.8 | 79 | 51 | 16.2 | 33 | 1425 | » | | |
| | 3. | 610 | 2.8 | 74 | 66 | 15.5 | 33 | 1350 | 340 | 95 | 565 |
| | 4. | 640 | 2.9 | 71 | 66 | 19.9 | 34 | 1425 | 348 | 75 | 540 |
| | | | | | Leached total amounts, mg from litre soil | | | | | | |
| Unlimed | | | | | 0.12 | 0.26 | 1.5 | 107 | | | |
| Limed | | | | | 8.53 | 10.55 | 3.9 | 163 | | | |

the treatment more from limed soil, 38 mg $l^{-1}$, than from unlimed soil, 22 mg $l^{-1}$, but the difference levelled off, reaching almost the same level at the end of the trial.

## DISCUSSION

In a laboratory experiment, ion transport was produced in a soil column by water percolation and upward impregnation in order to determine whether any changes had occurred. Similar transport of substances occurs in natural conditions, although the changes and chemical reactions in the laboratory are faster, e.g. because of the higher temperature.

The quantities of substances extracted in the experiment are affected by the oxidation and purification reactions which have previously occurred in the soil, these reactions being dependent on the moisture of the soil and the aerobic or anaerobic status of the soil. The oxidation or reduction events are further catalysed by microbia, made up of their own specific species in aerobic and anaerobic conditions. The leaching treatment applied in the experiment changed the moisture content of the entire soil column, and impregnation changed the moisture of the lower part of the soil column towards and anaerobic state as compared to native conditions. Apparently this is of significance when interpreting the concentrations measured in different layers after the experiment. In anaerobic conditions sulphate sulphur is reduced into sulphide, as can also be seen from the higher pH value measured in the dried soil.

The increase in the leached and also in the 0.6—1.0 m layer of impregnated soil profiles can be attributed mainly to the reduced $SO_4$-sulphur and to the increased soluble calcium contents. The presence of sulphate sulphur as sulphuric acid had maintained a low soil pH. Leaching of the soil had reduced the quantities of soluble salts, especially those of sulphate, which explains the decreased electric conductivity in the unlimed soil profile. The graphs describing the electric conductivity and sulphate concentration of untreated and leached soil are parallel both in unlimed and limed soil. A very good correlation, $r = 0.94^{***}$, was observed between sulphate sulphur and electric conductivity in sulphate soils collected from the drainage basin of the river Kyrönjoki, from which the soil samples had also been taken (ERVIÖ 1975).

A very high electric conductivity value of 46 $10 \times$ mS $cm^{-1}$ in the uppermost layer of the impregnation sample confirms that the soil water had a high salt content, which has risen to the surface through capillary force. The components of this salt, which crystallized onto this soil surface, have clearly been sulphate, calcium, magnesium, sodium, aluminium and manganese, but not potassium or iron. The slag alum crystallized onto the soil surface in the sulphate soils of Norrbotten, Sweden, was shown in most cases to contain mainly sulphate, aluminium, magnesium, manganese, in some cases also iron, but very little calcium, potassium and sodium (HANNERZ 1934).

Alum salts are so-called double salts, $M^{1+}\ M^{3+}(SO_4)_2 \times 12\ H_2O$, which also include a monovalent metal. In the present study, the monovalent cation was replaced mainly by sodium, because its concentration in the uppermost layer of the impregnated unlimed soil was tenfold the concentration of potassium (Fig. 2). The uppermost layer (0—0.1 m) of non-growing salt soil profile analysed by AARNIO (1924) near the town of Vaasa had concentrations mainly of sulphate, aluminium and calcium, but

the amount of potassium recovered was only one-tenth of the recovered quantity of sodium. HANNERZ (1934) showed alum in all three samples to contain clearly more sodium than potassium.

Liming of the experimental area 15 years earlier had enhanced the leaching of sulphate from the uppermost soil layer (0—0.6 m), as has been observed to occur in similar soils in Sweden (WIKLANDER et al. 1950). Thus, there was hardly any higher concentration of sulphate on the soil surface in the limed soil sample. Apparently for the same reason, less magnesium and manganese were recovered in the upper part of the limed soil profile than in the unlimed soil profile. Thus also less magnesium and manganese were concentrated in the soil surface.

The elevated pH, 5.5—6.5, in the anaerobic environment of the lower part of leached and impregnated soil profiles reduced the solubility of aluminium (RICHBURG and ADAMS 1970, ALLBROOK 1973). The elevated pH values of 3.7—4.3 seem to have already influenced the decrease of iron and manganese contents in the 0.6—0.8 m layer as compared to the concentrations in the original native soil (pH 3.3).

In all, a total of 163 mg of sulphur, 11 mg of aluminium, 9 mg of iron and 4 mg of manganese per litre of soil was leached from the limed profile. The quantities of leached elements correlated closely with the quantities of corresponding elements extracted by HARTIKAINEN and YLI-HALLA (1986) from the layer above the oxidation limit in acid sulphate soil S = 181, Al = 5, Fe = 3, and Mn = 2 mg $kg^{-1}$ soil.

The water leached from sulphate soils is detrimental for the fish and crustaceans in watercourses because of their very low pH and high sulphur, aluminium and iron concentrations. When calculated per hectare, approx. 1.600 kg of sulphur, 105 kg of aluminium and approx. 85 kg of iron were leached from a 1 m layer. The low pH (5.0) of water causes deaths of fish through destruction of the respiration epithelia of the gills. The toxicity of trivalent ferrisulphate is based on the fact that the water tends to reduce the pH. In addition, the soluble iron present in water is sedimented in the gills of the fish, causing suffocation. Aluminium sulphate has been shown to be toxic to several fish species. The present study indicates that clearly more sulphate sulphur, aluminium and iron were leached from the limed soil than from the unlimed soil.

*Acknowledgements* — I would like to thank Mr. Tauno Tares M.Sc. for the supervising of analyses in the laboratory of the Department of Soil Science.

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*Manuscript received July 1990*

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## SELOSTUS

# Huuhtoutumisen ja kapillaarisen nousun aiheuttama ionien liikkuminen savisessa happamassa sulfaattimaassa

RAIMO ERVIÖ

Maatalouden tutkimuskeskus

Happamat sulfaattimaat sisältävät runsaasti tehokasta viljelyä haittaavia suoloja, joita huuhtoutuu sateiden vaikutuksesta aikaa myöten pois, mutta joita myös nousee poutakausien aikana kapillaariveden mukana syvemmältä maan pintakerrokseen.

Jäljitellen luonnonoloja laboratorioissa suoritetussa, 30 viikkoa kestäneessä kokeessa selvitettiin ionien kulkeutumista maassa huuhtelun vaikutuksesta alaspäin ja haihtumisvirtauksen ja kapillaarivoiman vaikutuksesta ylöspäin. Koemaat otettiin Etelä-Pohjanmaalta Korsholman koulutilalta, Vaasan läheltä olleesta sulfaattimaan kalkituskokeesta, kalkitsemattomalta ja runsaan kalkituksen (32 tn $ha^{-1}$) saaneelta ruudulta.

Huuhtelun tai veden altaimeytyksen vaikutukset maan pintaosan pH-arvoon olivat vähäiset. Maan suolapitoisuutta ilmentävä johtoluku laski huuhtelun ansiosta niissä profiilin osissa, joissa se oli ollut yli 10.

Huuhtelun todettiin vähentäneen $SO_4$-, Mg- ja Mn-ioneja maan koko profiilin matkalta kalkitsemattomaan verrattuna sekä profiilin pintaosasta Ca- ja Al-ioneja. $SO_4$, Mg ja Mn vähenivät myös kalkitun maan profiilin alaosasta (alle 0.6 m), jossa pitoisuudet olivat pintamaita selvästi suuremmat. Huuhtelu näytti sitävastoin lisänneen uuttuvan kaliumin määrää profiilin keskiosaa lukuunottamatta sekä kalkitsemattomassa että kalkitussa maassa ja raudan määrää profiilin pintaosassa.

Maanesteen kapillaarinen kulkeutuminen ylöspäin toteutettiin lieriössä, jonka pinnasta veden annettiin haihtua alapään ollessa veden alla. Koejakson kuluessa oli kalkitsemattoman maan pintaosaan (0—3 cm) rikastunut erittäin selvästi Ca-, Mg-, Na-, Mn-, Al- ja $SO_4$-ioneja, mutta ei K- eikä Fe-ioneja. Kalkitun maan pintaan kerääntyi selvästi Ca- ja Mg-ioneja, niukasti Na-, Mn- ja $SO_4$-ioneja, mutta ei lainkaan K-, Fe- ja Al-ioneja. Lisäksi olivat Ca-, Mg-, Na-, Mn- ja $SO_4$-ionit lisääntyneet 0.2—0.4 tai 0.4—0.6 m:n kerroksissa varsinkin kalkitussa maassa verrattuna alkuperäisen profiilin pitoisuuksiin.

Altaimeytyksessä tapahtuneen suolojen rikastumisen seurauksena maan pintaosan johtoluku oli kokeen lopussa 46 kalkitsemattomassa maassa ja 17 kalkitussakin maassa, kun se huuhdellussa maassa oli molemmissa tapauksissa ainoastaan 5.

Maapatsaan läpivalutetun veden pH-arvo nousi kalkitsemattomalla maalla huuhtelun aikana pH 3.9:stä pH 4.7:ään johtoluvun ollessa noin 100, mutta kalkitulla maalla pH pysytteli arvon 3 alapuolella ja johtoluku laski 90:stä 70:een. Sekä rautaa että alumiinia huuhtoutui kalkitsemattomasta maasta selvästi enemmän kuin kalkitusta maasta, mutta mangaania sitä vastoin kalkitusta maasta enemmän nimenomaan koejakson alkupuolella. Huuhtoutuneen Al:n ja Fe:n määrät putosivat yleensä toistettujen huuhtelukertojen myötä.

Kahden viimeisen kerran huuhdenäytteiden Ca-konsentraatio oli kalkitsemattoman maan vedessä sama ja K- sekä Mg-konsentraatio kaksinkertainen kalkittuun nähden.

Sulfaattirikkiä huuhtoutui kalkitsemattomasta maasta koko koejakson ajan sama määrä, noin 2 000 mg, mutta kalkitusta maasta sen määrä oli vähäisempi ja laski kokeen jatkuessa. Koemaa sisälsi sulfaattirikkiä keskimäärin noin 2 000 mg $l^{-1}$ maata. Koejakson aikana huuhtoutui kalkitsemattomasta maalitrasta $SO_4$-rikkiä 107 mg, mikä on vain noin 19. osa koko tutkitussa maassa todetusta sulfaattirikkimäärästä.

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 331—344 (1991)
Seria AGROGEOLOGIA ET -CHIMICA N. 161 — Sarja MAA JA LANNOITUS n:o 161

# ACID-INDUCED LEACHING OF ELEMENTS FROM CULTIVATED SOILS

RAIMO ERVIÖ

ERVIÖ, R. 1991. Acid-induced leaching of elements from cultivated soils. Ann. Agric. Fenn. 30: 331—344. (Agric. Res. Centre of Finland, Inst. Crop and Soil Sci., SF-31600 Jokioinen, Finland.)

Four types of arable soil were leached in the experiment — sand, silt, clay and peat — using irrigation water of pH 5.7, 5.0, 4.5, 4.0 and 3.5 adjusted by means of $H_2SO_4$. Irrigation was carried out at a level of 30 mm once a week, the total amount of water given over a period of 18 weeks corresponding to the mean annual precipitation in Finland.

The pH of the leachate clearly increased during the course of the experiment, apart from the sandy soil where the pH remained constant. The leaching of Ca, Mg, K, Na, Zn and S was highest during the first 5—7 irrigation episodes.

The most acidic irrigation water (pH 3.5) leached during different irrigation episodes more only Ca and Mg from all types of soil, and K from the sandy soil and Na from the clay than what was leached by the irrigation waters with higher pH. The total amount of Mg leaching from all types of soil increased when irrigated with the pH 3.5 water, Ca leaching from the sand and clay, K from the sand and silt, and Na and B from the clay. In contrast, the leaching of Al by the most acidic irrigation water was lowest from the silt, clay and peat soils. There were no clear differences in the total leaching of other elements (P, Mn, Cu, Fe, Zn) between the irrigation treatments.

No differences were found at the end of the experiment between the irrigation treatments as regards the contents of plant available nutrients and heavy metals in the soil, the pH nor neutral ammonium acetate exchangeable base cations.

Index words: arable soil, irrigation, leachate, acidic water, pH, calcium, potassium, magnesium, sodium, phosphorus, sulphur, aluminium, iron, copper, zinc.

## INTRODUCTION

During the past two decades coniferous forest decline has been observed in Central Europe and in North America. The cause of the damage has been attributed to air pollution, primarily sulphur deposition. Other suspected causal agents include heavy metals, nitric oxides, ozone, a deficit of carbon dioxide and increased UV radiation. Since sulphur and nitrogen are converted in the atmosphere into strong acids, they are assumed to bring about a decrease in soil pH when they are carried down into the ground by precipitation. The increase in the hydrogen ion concentration in the soil solution results in the displacement of base cations from the exchange sites on the soil particles, and their subsequently leaching. Further increases in the hydrogen ion concentration causes weathering of the mineral material and an in-

crease in soluble aluminium concentrations. This may have a toxic effect on the development of plant roots.

In addition to forest soil acidification, there is also increasing suspicion that arable soils are becoming acidified. A study was carried out in which different types of arable soil were treated with irrigation water acidified to varying degrees with sulphuric acid. The amount of hydrogen ions in the most acidic irrigation water (pH 3.5) was equivalent to the hydrogen ion load in bulk precipitation in southern Finland over a ten-year period.

## MATERIAL AND METHODS

Four types of arable soil from southern Finland were chosen for the experiment: sand, silt, clay and peat (Table 1). The fine sand and silt was taken from a site polluted by the metal industry because the aim was also to determine the possible effects of acidic irrigation on the leaching of some heavy metals.

Seven litres of soil were placed in a 20 cm thick layer in plant culture pots (Kick-Brauckmann). The leachate passing through the soil

Table 1. The properties of the soils used.

| Soil | Bulk density | Organic carbon (%) | Particle size distribution | | | | pH | | Electric conductivity mS/cm |
|---|---|---|---|---|---|---|---|---|---|
| | | | clay <2 μ | silt 2—20 μ | fine sand 20—200 μ | sand >200 μ | ($H_2O$) | ($CaCl_2$) | |
| Sand | 1.20 | 2.1 | 3 | 8 | 30 | 59 | 6.45 | 5.80 | 0.9 |
| Sandy silt | 1.03 | 2.4 | 17 | 47 | 24 | 12 | 5.50 | 4.80 | 1.2 |
| Sandy clay | 0.96 | 3.1 | 49 | 29 | 13 | 9 | 6.15 | 5.50 | 0.8 |
| Peat | 0.40 | 30.0 | — | — | — | — | 5.00 | 4.75 | 6.0 |

| Soil | Exchangeable cations meq/100 g soil | | | | | | Base saturation % |
|---|---|---|---|---|---|---|---|
| | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Na^+$ | $H^+$ | CEC | |
| Sand | 4.5 | 1.4 | 0.1 | 0.2 | 8.0 | 14.2 | 44 |
| Sandy silt | 4.8 | 1.1 | 0.9 | 0.2 | 12.0 | 19.0 | 37 |
| Sandy clay | 11.9 | 4.0 | 0.8 | 0.3 | 12.0 | 29.0 | 59 |
| Peat | 24.0 | 4.9 | 0.2 | 0.3 | 44.0 | 73.4 | 40 |

| Soil | B mg/l | AAAc-extractable elements mg/l soil | | AAAc-EDTA extractable mg/l soil | | | | |
|---|---|---|---|---|---|---|---|---|
| | | P | S | Al | Cu | Fe | Mn | Zn |
| Sand | 0.3 | 20 | 13 | 354 | 141 | 435 | 19 | 12 |
| Sandy silt | 0.6 | 12 | 42 | 316 | 162 | 483 | 98 | 16 |
| Sandy clay | 0.8 | 13 | 19 | 265 | 6 | 627 | 76 | 2 |
| Peat | 0.9 | 2 | 44 | 629 | 3 | 276 | 61 | 2 |

was collected in bottles.

The pH values of the irrigation water were obtained as follows:

| | | |
|---|---|---|
| 1. | pH 5.7 | deionized water, saturated by aeration with $CO_2$ |
| 2. | 5.0 | 0.14 ml 0.1 N $H_2SO_4$ added into 1 l water |
| 3. | 4.5 | 0.45 » » » » » » |
| 4. | 4.0 | 1.40 » » » » » » |
| 5. | 3.5 | 4.30 » » » » » » |

The actual pH values of the irrigation water, monitored weekly, were: 1) 5.62—5.84, 2) 4.90—4.98, 3) 4.39—4.50, 4) 3.89—3.95 and 5) 3.41—3.47.

There were 4 soils, 5 treatments and three replications ($4 \times 5 \times 3 = 60$). The pots were kept in a room where the mean temperature during the experiment was + 17 °C (range 15—20 °C).

The total amount of irrigation water applied was calculated to be equivalent to the mean annual precipitation in Finland (550 mm). Before leaching episodes the soils were moistened to field capacity. The water was added to the pots once a week at a rate of 1 070 ml/pot during a period of 18 weeks. The water was carefully poured into the pots at one go. The leachate was removed once a week for analysis before the next irrigation episode.

The pH and electrical conductivity of the leachate were measured immediately. 50 ml of 6 N HCl/l was added to the leachate for storage. At the end of the experiment all the leachate samples were analysed concurrently by inductively coupled plasma atomic emission spectrometry (ICP/AES) for the following elements (Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn.

At the end of the experiment soil samples were taken at six points in each pot with a soil auger pushed down to the bottom of the pot. The samples were dried and then milled to pass through a 2-mm sieve. Soil pH($H_2O$) and electrical conductivity were measured from a water/soil slurry (1:2.5), and pH($CaCl_2$) using a 0.01 M $CaCl_2$ solution in the same proportions. Plant available nutrients were determined by extraction with 1 M acidic ammonium acetate (AAAc), pH 4.65 (Ca, K, Mg, Na, P and S) (VUORINEN and MÄKITIE 1955), or with $NH_4$-OAc-EDTA (Al, Cu, Fe, Mn) (LAKANEN and ERVIÖ 1971) in the ratio 1:10. The elements were determined by ICP/AES. Boron was determined following extraction with water (SIPPOLA and ERVIÖ 1977). The potential cation exchange capacity was determined by extraction with neutral ammonium acetate (ANON. 1986), and calculated as the sum of equivalent contents of basic cations (Ca, Mg, K, Na) and titratable acidity.

## RESULTS

The pH electrical conductivity of the leachate obtained with the most acidic irrigation water during the course of the 18-week experiment are presented in Figs. 1 and 2. The pH of the leachate from the peat increased relatively the most: from 5.0 after the first irrigation episode to 6.7 after the 17th. The pH of the irrigation water had no effect on this trend. The pH of the leachate from the silt and clay increased from about 6.0 to over 7.9, and from about 6.7 to 7.9, respectively. The increase was the strongest from the beginning of the experiment to the 7th irrigation episode. The pH of the leachate from the sandy soil remained at approximately the same level throughout the experiment, varying only from 7.3 to 7.5, irrespective of the pH of the irrigation water.

The electrical conductivity of the leachate fell

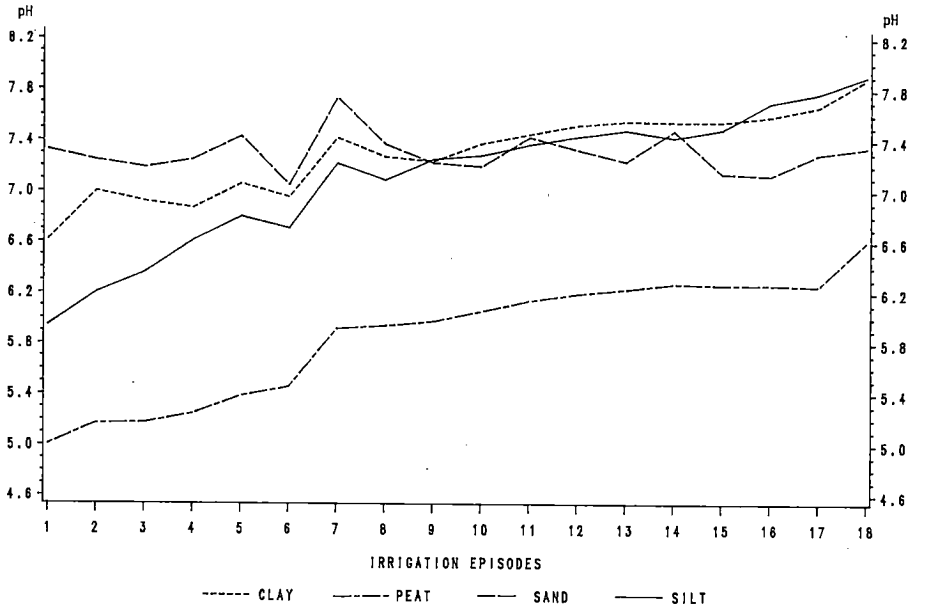


Fig. 1. pH-values of leachates from experiment soils irrigated with pH 3.5 leaching water.

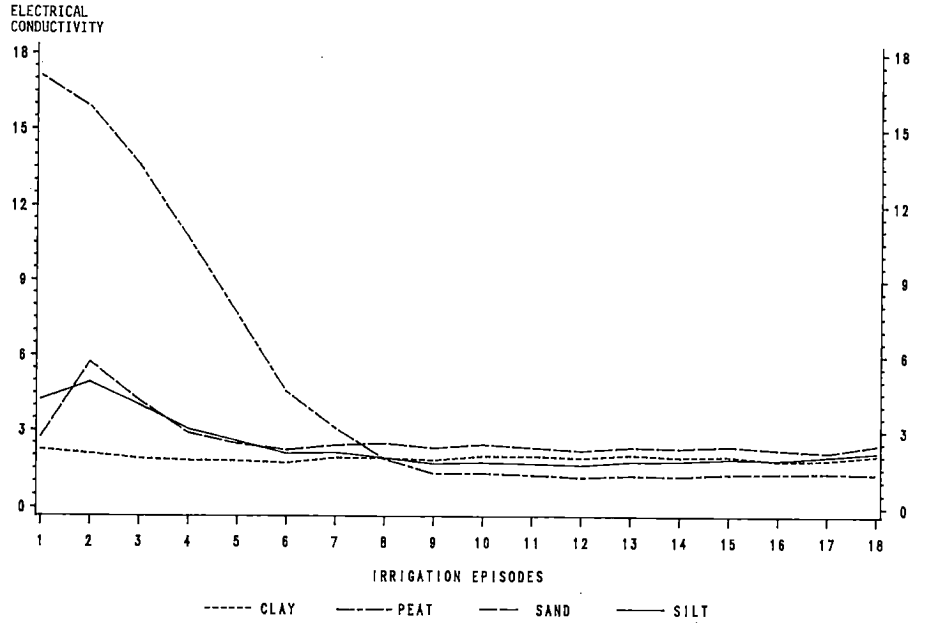


Fig. 2. Electrical conductivity values of leachates from soils during experiment time.

from the third irrigation episode to the 5th in the case of the sand and to the 9th in the case of the silt and peat, and then remained relatively constant to the end of the experiment. However, the electrical conductivity of the leachate from all types of soil in the latter half of the ex-

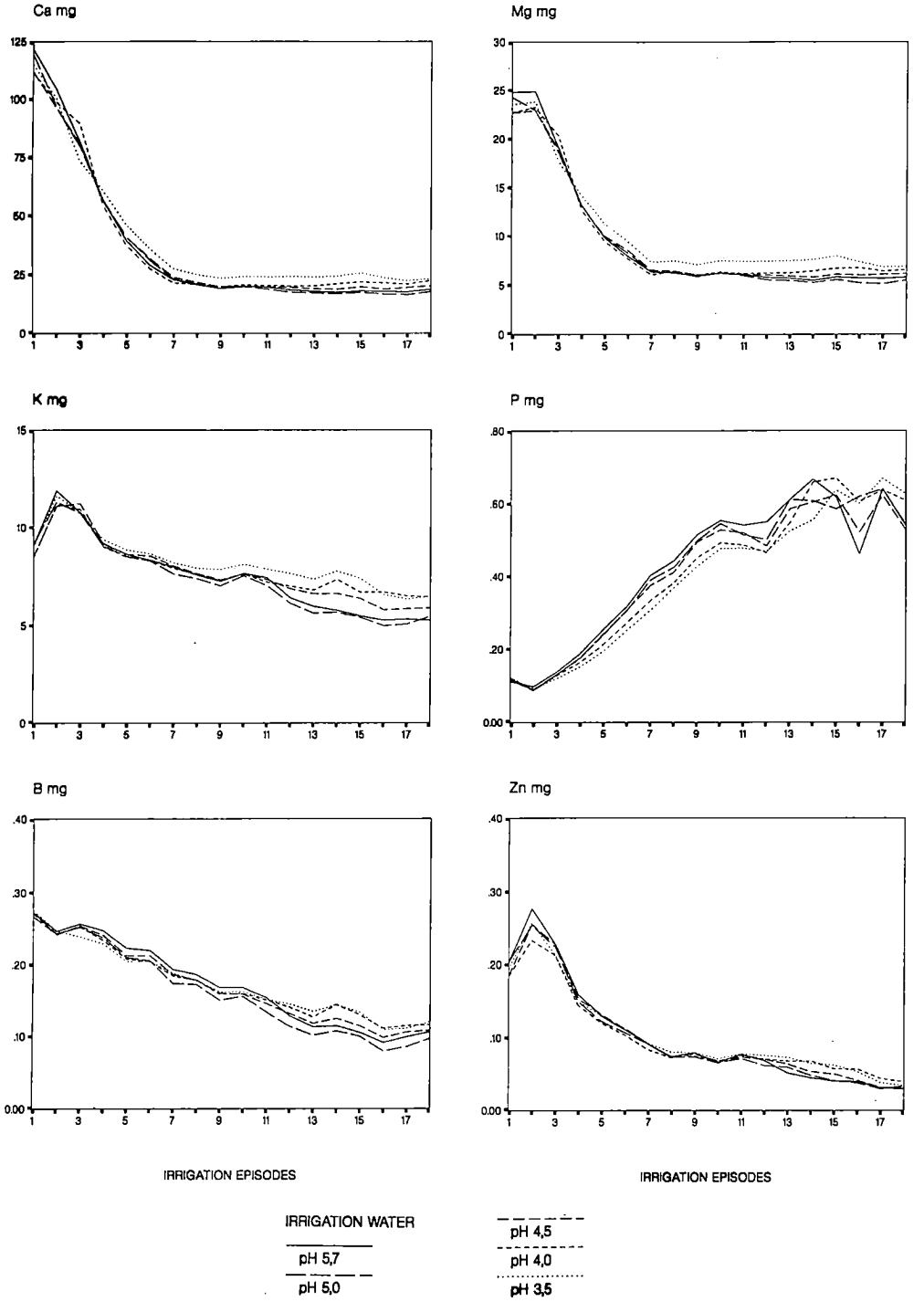


Fig. 3. The average element amounts, mg, from all experiment soils leached by different acid irrigation waters in various irrigation episodes.

periment was higher with the pH 3.5 irrigation water than the other irrigation treatments. There was variation in the sulphur concentrations of the leachate between subsequent irrigation episodes, but the electrical conductivity of the leachate from the pots receiving the highest amounts of sulphuric acid remained higher than the others.

Calcium was leached in the greatest amounts during the first few irrigation episodes: from the clay during the first two, from the sand during the first four, and from the silt and peat during the first seven. Leaching continued to the end of the experiment at a rather constant level (Fig. 3). The greatest amount of Ca in the leachate, over 200 mg, occurred at the beginning of the experiment from the peat. The amount of Ca in the leachate levelled off to 10 mg from the peat, to below 20 mg from the clay and silt, and to below 30 mg from the sand.

The most acidic irrigation water leached more Ca than the other irrigation treatments in the case of all types of soil starting from after the 8th or 9th irrigation episode. The most regular difference occurred with the clay: the Ca concentration with pH 3.5 water was about 20 mg, and with pH 5.0 water about 10 mg. A similar result was obtained with the silt only between the 13th and 16th irrigation episodes, with the peat between the 9th and 16th, and with the sand between the 8th and 15th.

Potassium was leached in the greatest amounts during the first irrigation episode (Fig. 3). More K was leached from the sand with the most acidic irrigation water (pH 3.5) than treatments with pH 5.7, 5.0 and 4.5 between the 8th and 14th irrigation episodes. There were only random differences with the other types of soil, and the smallest difference in the case of the peat. The leaching of K from the clay with the most acidic irrigation water remained at about the 10 mg level, and fell in the case of the other types of soil to about one third of the initial level.

Magnesium was also leached in the greatest amounts after the first few irrigation episodes, and in a very similar fashion to Ca from all experiment soils (Fig. 3). From clay most Mg was leached after the first two, from sand after the first four and from silt and peat after the first seven episodes. In the case of clay the most acidic irrigation water (pH 3.5) clearly leached more Mg than the pH 5.0 water. The amounts of Mg leached from the sand by the pH 3.5 water differed during part of the experiment (5th to 15th irrigation episodes). There were no regular differences between the amounts of Mg leached from the silt by the different irrigation treatments. More Mg was leached from the peat by the pH 3.5 irrigation water than by the less acidic treatments. In the case of the clay the amount of Mg leaching remained at the 5—7 mg level throughout the experiment, but with sand and silt it fell to about one third of the level during the early stages of the experiment and with peat to about one tenth.

Sodium was leached in large amounts at the beginning of the experiment in the same way as the other basic metals. However, the fall from the initial high level was less steep. The reduction continued up until the end of the experiment, apart from the peat where leaching levelled off after the 9th irrigation episode. There were no clear differences between the ability of the different irrigation treatments to leach Na, apart from clay between the pH value of 3.5 and the pH values of 4.0 and 5.0 after a few of the irrigation episodes towards the end of the experiment. In the case of clay the leaching of Na decreased with increasing number of irrigation episodes to about one half, in the case of sand and silt to about one third, and for peat to about one fifth.

Phosphorus leaching in general increased during the course of the experiment, the mean leaching level for the whole material being triple the level at the end of the experiment as compared to the initial level (Fig. 3). The clearest increase in P leaching occurred from the sand. The pH 5.7 irrigation water leached

more P from the clay and silt after a number of irrigation episodes than the pH 3.5 and pH 4.0 water. In contrast, pH 4.0 water was more effective in leaching P from the peat than the pH 3.5 water. Phosphorus leaching from clay and peat was about double by the end of the experiment, from silt about triple and from sand about ninefold as compared to the initial level.

Boron leaching in general decreased after each successive application of irrigation water. The only clear difference between the irrigation treatments occurred after a few irrigation episodes approximately half way through the experiment: between pH 5.7 and pH 4.0 and 3.5 irrigation water. The higher the pH of the irrigation water, the more effective was leaching (Fig. 3). Boron leaching fell the steepest in the case of the silt: initially it was about 0.4 mg and at the end of the experiment 0.1 mg. The drop for the other types of soil was from 0.2 to 0.1 mg.

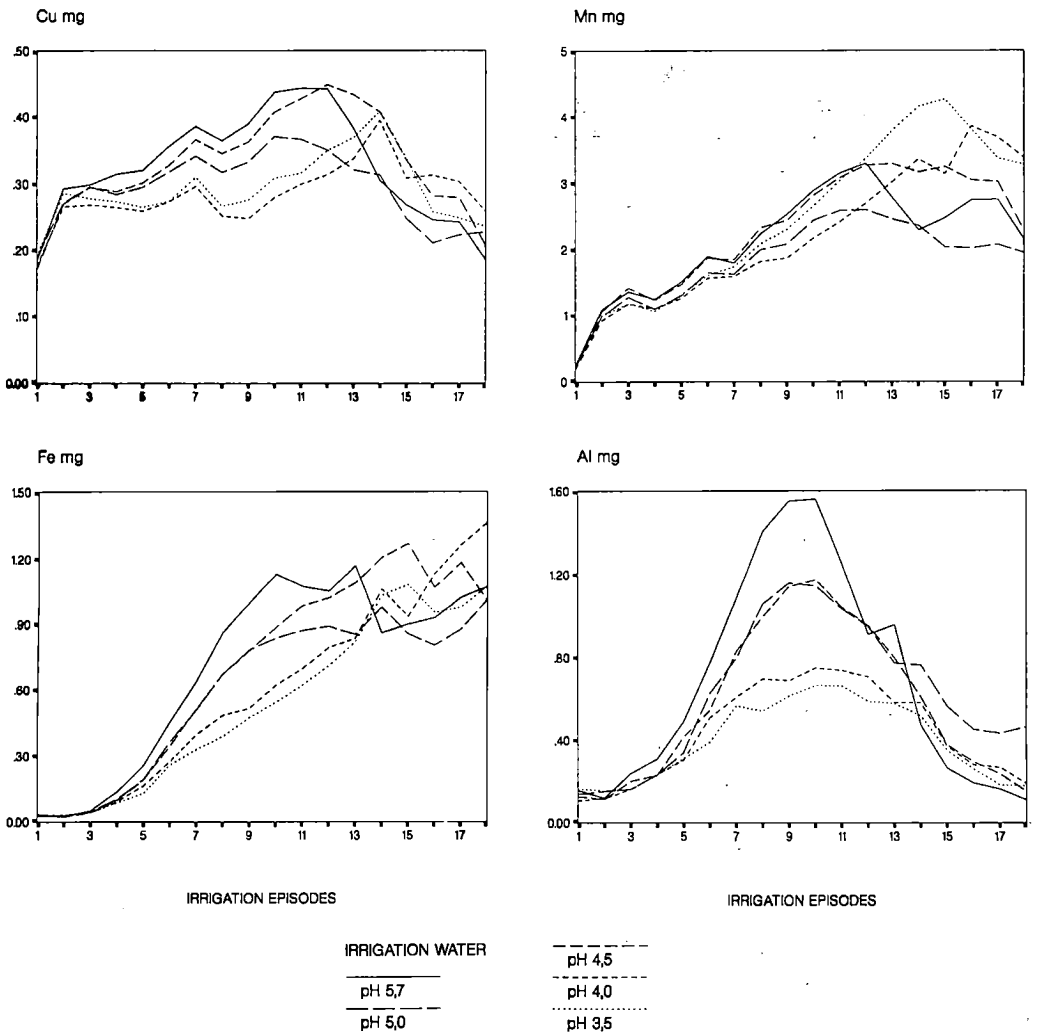


Fig. 4. The average element amounts, mg, from silt soil leached by different acid irrigation waters in various irrigation episodes.

Copper leaching increased up until the 12th irrigation episode from the sand and the silt soil that contained exceptionally high levels of Cu. There were no clear trends in the case of the clay and peat soil. More Cu was leached only from the silt with pH 5.7 irrigation water than with pH 4.0 and 3.5 irrigation water halfway through the experiment (Fig. 4). Leaching levels from the sand were eight times higher and from the silt double, but then fell to the level obtained after the first few leaching episodes. The amount of Cu leached from the clay and peat remained at approximately the same level throughout the experiment.

Zinc leaching resembled that of the basic elements (Fig. 3). Leaching was greatest after the first few irrigation episodes and then fell sharply after the 5th from the sand, after the 8th from the peat and after the 10th irrigation episode from the silt. Leaching from the sand fell even more clearly from the 11th to the 17th irrigation episode. There were no differences between the irrigation episodes as regards leaching intensity from the clay. The amounts of Zn leached from the sand fell to about one fifth, from the peat to about one sixth and from the silt to about one quarter of the level at the start of the experiment.

There were no clear differences in leaching intensity between the irrigation treatments. Zinc leaching from the sand only was greater after the last few irrigation episodes with the most acidic irrigation water than with the other treatments.

Manganese leaching from the different types of soil varied considerably. In general, leaching from the clay and silt increased throughout the course of the experiment: in the case of silt 3—6 times (Fig. 4). Mn was leached from the peat during the first 8 irrigation episodes, and then fell to approximately the same low level (one seventeenth of the initial) for the rest of the experiment. Leaching from the sand was greatest during the middle of the experiment.

Greater acidity of the irrigation water increased the amount of Mn leached from the peat only during a few irrigation episodes halfway through the experiment, and from silt during the last few episodes. More Mn was initially leached from the clay with the pH 5.7 irrigation water than with the pH 3.5 water, but after the 11th irrigation episode the pH 3.5 water leached more than the pH 5.0 water.

Iron leaching increased from all types of soil as the experiment proceeded. Leaching from the clay increased sharply up until the 5th irrigation episode, from the silt, sand and peat gradually up until the 12th, and then more steeply. Iron leaching increased the least during the experiment from the clay (2—5 times). The increase was 5—10 times from the peat and about 10 times from the silt. The most acidic water (pH 3.5) leached Fe the least from the clay and silt (Fig. 4), and pH 4.0 water the most from the peat. There were no clear differences between the effects of the other irrigation treatments.

Aluminium leaching increased from all types of soil during the first half of the experiment, from clay up until the 6th, and from silt, sand and peat up until the 10th irrigation episode. Aluminium leaching subsequently decreased the most clearly from the silt and sand. The pH 5.7 water leached the most Al from the clay and silt, and the pH 4.0 water from the peat. The difference between these types of soil was clear especially with respect to the amount of Al leached by the pH 3.5 water during irrigation episodes in the middle of the experiment. The pH 4.0 water more effectively leached Al from the peat than the pH 3.5 water. The amounts of Al leached during the middle of the experiment were 3—4 times higher than those at the beginning. However, the amount of Al leached fell as irrigation was continued, and in the case of the silt almost to the initial level (Fig. 4).

Sulphur leaching decreased sharply at the beginning of the experiment with all irrigation treatments, and gradually towards the end of the experiment, apart from the pH 3.5 water

with the clay where S leaching remained almost constant throughout the experiment. The amount of S leached was naturally higher in the treatments involving the addition of sulphuric acid. During the course of the experiment S leaching from the clay fell to about half the starting level and from the other soils to about 1/8.

## Total leaching

The total amount of elements leached was primarily dependent on the soil type, and on its binding properties and contents of easily exchangeable elements, but not very much on the acidity of the irrigation water. Irrigation water pH hardly had any effect on the total amounts of Na, P, B, Fe, Cu and Zn leached during the experiment (Table 2).

The most acidic irrigation water (pH 3.5) clearly increased total leaching of Ca from the sand and clay, Mg from the sand and to some extent from the clay, silt and peat, K only from the sand and silt, Mn only from the sand, and B only from the clay. In turn, pH 3.5 water decreased the total leaching of Al from the silt, clay and peat, B from the peat, and P from the silt. A clear increase in the leaching of the S given in the irrigation water occurred from all types of soil with the pH 3.5 water and, apart from the silt, also with the pH 4.0 water.

## Changes in the leached soils

At the end of the experiment the soils were analysed for pH, electrical conductivity, plant-available nutrients and heavy metals, and base cations displaced by neutral ammonium acetate. No statistically significant changes were found between the effects of the irrigation treatments on these soil parameters (Fig. 5). The only understandable change was the increase in the S content of the soils as a result of the sulphuric acid addition to the irrigation water.

There were not even any differences in pH($H_2O$) or pH($CaCl_2$), nor in the neutral am-

Table 2. The total leakages (mg) of elements from seven liter soil after 18 leaching episodes. (Different index letters indicate statistical significant differences.)

| Soil | Treatment | Ca | Mg | K | Na | P | B | Al | Fe | Cu | Zn | Mn | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sand | pH 5.7 | $539_a$ | $239^a$ | $172^a$ | 26 | 21.43 | 1.94 | 13 | 93 | 14.7 | 1.03 | $9.3^a$ | $108^a$ |
| | 5.0 | $538^a$ | $239^a$ | $172^a$ | 26 | $21.56^a$ | 2.02 | 13 | 91 | 14.6 | 1.09 | $10.0^a$ | $111^a$ |
| | 4.5 | $527^a$ | $233^a$ | $170^a$ | 26 | 20.07 | 1.92 | 13 | 78 | 14.5 | 1.07 | $9.4^a$ | $114^a$ |
| | 4.0 | $527^a$ | $236^a$ | $172^a$ | 26 | $19.49^b$ | 1.98 | 12 | 76 | 14.6 | 1.08 | $9.2^a$ | $129^b$ |
| | 3.5 | $610^b$ | $273^b$ | $188^b$ | 26 | 20.56 | 1.96 | 13 | 109 | 14.4 | 1.11 | $13.1^b$ | $161^c$ |
| Silt | pH 5.7 | 419 | 103 | $156^a$ | 54 | $2.87^a$ | 4.64 | $12^a$ | 13 | 5.9 | 4.9 | 38.4 | $361^a$ |
| | 5.0 | 401 | $97^a$ | $155^a$ | 53 | $2.73^a$ | 4.54 | 11 | 11 | 5.3 | 4.8 | 32.8 | $351^a$ |
| | 4.5 | 429 | 105 | 163 | 55 | $2.80^a$ | 4.67 | 10 | 12 | 6.0 | 4.9 | 41.1 | $375^a$ |
| | 4.0 | 408 | 99 | $160^a$ | 52 | 2.45 | 4.50 | 8 | 11 | 5.1 | 4.7 | 39.2 | $373^a$ |
| | 3.5 | 457 | $112^b$ | $173^b$ | 55 | $2.37^b$ | 4.64 | $7^b$ | 10 | 5.2 | 5.2 | 44.2 | $431^b$ |
| Clay | pH 5.7 | $286^{ab}$ | 96 | 175 | 71 | 4.37 | 3.07 | $107^a$ | $69^a$ | .33 | .33 | 1.0 | $95^{ac}$ |
| | 5.0 | $252^a$ | $85^a$ | 163 | $62^a$ | 3.86 | $2.42^a$ | $91^a$ | $59^a$ | .32 | .26 | 0.6 | $89^{ab}$ |
| | 4.5 | $304^{ab}$ | 101 | 186 | 72 | 4.42 | 3.04 | $105^a$ | $67^a$ | .35 | .32 | 0.9 | $107^c$ |
| | 4.0 | $327^{bc}$ | $108^b$ | 194 | $77^b$ | 4.54 | $3.35^b$ | $109^a$ | $70^a$ | .37 | .33 | 0.8 | $134^d$ |
| | 3.5 | $371^c$ | $112^b$ | 189 | $77^b$ | 3.54 | $3.41^b$ | $54^b$ | $33^b$ | .31 | .25 | 1.0 | $203^e$ |
| Peat | pH 5.7 | 1 399 | 243 | $37^a$ | 56 | 1.93 | $2.73^a$ | 23 | 31 | .35 | .95 | 20.1 | $205^a$ |
| | 5.0 | 1 391 | 241 | $37^a$ | 55 | 2.00 | 2.60 | 22 | 35 | $.31^a$ | $.91^a$ | 20.2 | $205^a$ |
| | 4.5 | 1 372 | $238^a$ | $37^a$ | 55 | 2.14 | 2.62 | 23 | 43 | .36 | $.90^a$ | 20.4 | $212^a$ |
| | 4.0 | 1 418 | 246 | 39 | 57 | 2.83 | 2.68 | $27^a$ | 71 | $.38^b$ | $1.04^b$ | 22.3 | $239^b$ |
| | 3.5 | 1 451 | $255^b$ | $40^b$ | 57 | 1.81 | $2.55^b$ | $20^b$ | 36 | $.32^a$ | $.92^a$ | 22.5 | $305^c$ |

monium acetate exchangeable base cations. The change in the mean pH($CaCl_2$) of all the soils between the pH 3.5 and pH 5.7 water was 0.033 pH-units.

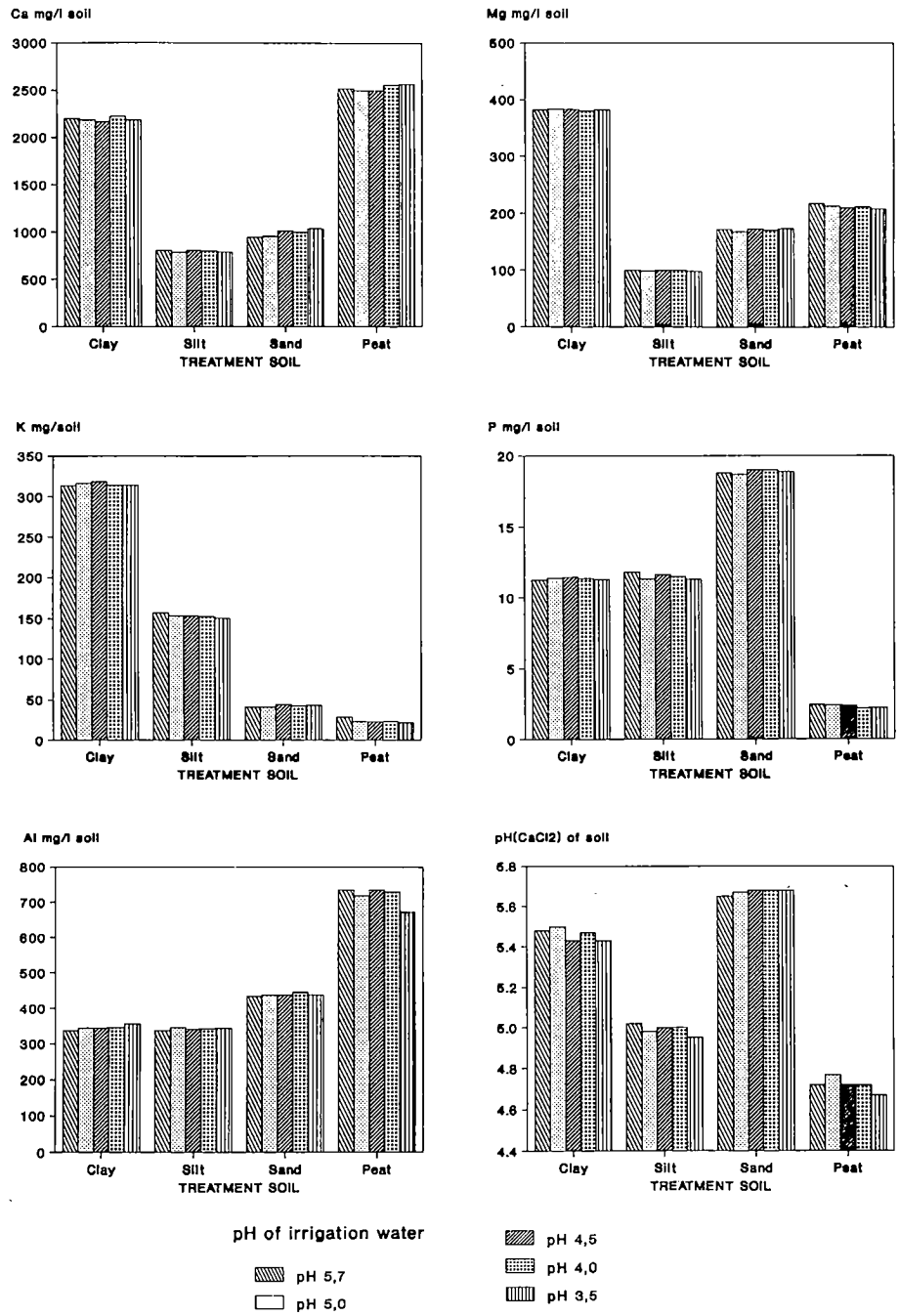


Fig. 5. The contents of elements and the pH in the soils after irrigating with acidified waters.

In studies carried out with irrigation water where the pH was adjusted using sulphuric acid, the amounts of basic cations (Ca, Mg, K, Na) leached increased with increasing acidity of the irrigation water and the longer the duration of the irrigation treatments (TEIGEN et al. 1976, HARTIKAINEN 1978, ABRAHAMSEN 1980, BJOR and TEIGEN 1980, HEAGLE et al. 1983, NISSINEN and ILVESNIEMI 1990). However, the pH of the irrigation water has had to be at least 3, in many cases even below, before such base cation leaching can be demonstrated with any statistical certainty (OVERREIN 1972, HAUGBOTN 1976, HAMAN 1977, ABRAHAMSEN and STUANES 1986, MACDONALD et al. 1986, CARLSON and RAGSDALE 1988). SINGH et al. (1980) did not find any differences in the leaching of basic cations from a podzolic soil when the pH of the irrigation water was 5.6 or 4.3. According to results of BERGKVIST (1986) irrigation water of pH 3.0 leached more calcium and magnesium but not potassium and natrium than irrigation water of pH 3.3 from horizons $A_o$, A and A-B of podzol soil.

The most acidic irrigation water used in this experiment was 3.5, and had a hydrogen concentration equal to ten times that in precipitation in southern Finland (JÄRVINEN and VÄNNI 1990). Only the pH 3.5 irrigation water caused any significant differences in the amounts of Ca and Mg leached from all the soil types after five irrigation episodes compared to the pH 5.7 and pH 5.0 water. A corresponding difference in K leaching was obtained only from the sandy soil, and for Na only the clay soil. Also NISSINEN and ILVESNIEMI (1990) found that the leaching of K from forest humus and eluvial layers' soil did not depend on the pH of treatment solution, even though with Ca and Mg so was happened.

An increase in the pH of the leachate with increasing irrigation episodes was observed from the clay, silt and peat, but not from the sand. The basic cations leached during irrigation caused the pH-increase of the leachate. The result was not dependent on the pH of the irrigation water. MCCLENAHEN (1987) did not find any differences in leachate pH in an experiment with forest soil using irrigation water pH values of 6.0 and 4.0. In POPOVIC's (1986) experiment, the leachate pH from an iron podzolic soil did not fall until the third year of irrigation when the irrigation water pH was 3.0. In STUANES' (1984) experiment the leachate pH was found to fall when the irrigation water was 3.8, but to increase when the irrigation water pH was 4.3 and 5.3. In a lysimeter experiment with an iron podzol, and irrigation water of pH 2.5 and 3.0, the pH values of the leachate fell in comparison to the leachate obtained with water of pH 5.3 and 4.0. In the latter cases there were no changes in leachate pH after irrigation with 5 000 mm of water (BJOR and TEIGEN 1980). HAY et al. (1985) did not find any noticeable changes in leachate pH when over 900 mm of irrigation water of pH 2.0 and 3.5 were passed through a podzol during a 16-day period.

In general there were no clear differences in the total leaching of P and Al between the irrigation treatments. The leaching of P from the sandy soil was less with the pH 3.5 treatment than the pH 5.0 water. Less Al was leached from the clay by the pH 3.5 treatment than all the other treatments, from the silt less with the pH 3.5 treatment than the 5.7 water and from the peat by the pH 3.5 treatment than the pH 4.0 water. Similarly, JOHNSON and TODD (1984) in an irrigation field experiment with $H_2SO_4$ and $HNO_3$ treatments found that pH 3.0 water did not cause any consistent increase in P and Al leaching compared to irrigation with distilled water. BERGKVIST (1986) also observed that release of Al and Fe did not seem to be enhanced at all by the acidity added to the podzol soil. However, in PÄTILÄ's (1990) irrigation experiment the water of pH 2 leached aluminium from the *Sphagnum* peat more than the irriga-

tion waters of pH 3 or pH 4.

No significant change was found in the pH($H_2O$) or pH($CaCl_2$) of any of the soil types at the end of the irrigation experiment. However, experiments with irrigation water pH lower than that used here have brought about changes in soil pH. STUANES (1980) found that the total acidity of the soil changed only slightly with irrigation water of pH 6.0—3.0, but clearly fell when the irrigation water pH was below 3.0. In MacDONALD et al.'s (1986) studies the pH of the surface soil (0—5 cm) fell when the irrigation water pH was 3.0, but not when it was 4.0. Neither did the pH of deeper soil layers (5—10 or 10—15 cm) change even though the irrigation water pH was 2.5 or 2.0. HEAGLE et al. (1983) also observed that irrigation with water of pH 2.4 decreased the soil pH, but not pH 3.2 water. The pH 3 irrigation solution used by LEE (1985) decreased the soil pH and Ca and Mg concentrations, but not the K and Na concentrations nor the cation exchange capacity. The pH values decreased 0.5—0.7 unites after 16 months' irrigation at pH 2 water in *Sphagnum*- and *Carex* peat profiles but not at pH 3 or pH 4 water (PÄTILÄ 1990).

According to the results it is not likely, that acid rain with a pH of 4.5 could result in a measurable lowering of pH of arable land even during a time span of few tens of years. The increase in hydrogen ion concentration caused by heavy nitrogen fertilization is tenfold compared to the effect of rain water. The liming of arable land according to the normal management practice neutralizes these effects easily. Even the irrigation water with pH of 3.5 used in the study and which is tenfold in hydrogen ion concentration compared to rainwater, did not cause a significant lowering of pH in any experimental soil.

The total leaching of nutrient elements calcium, magnesium and potassium increased in some of experimental soils only when the most acid, pH 3.5 irrigation water was used. It is not likely that even in Southern Finland the acidity of rain water would in future decrease to that level.

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*Manuscript received January 1991*

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## SELOSTUS

# Huuhteluveden happamuuden vaikutus viljelymaasta huuhtoutuvien alkuaineiden määriin

RAIMO ERVIÖ

Maatalouden tutkimuskeskus

Rikkihapolla happamaksi tehtyjä vesiä valutettiin koeastioissa 20 cm:n maakerroksen läpi tarkoituksena selvittää maan kemiallista muuttumista ja läpivaluneen veden huuhtomien alkuaineiden määriä. Neljää maalajia hiekkaa, hiesua, savea ja turvetta huuhdeltiin pH 5,7:n ja happamiksi tehtyjen vesien (pH 5,0; 4,5; 4,0 ja 3,5) liuoksilla. Vettä valutettiin kerran viikossa 30 mm:n sadetta vastaava määrä 18 viikon ajan veden kokonaismäärän vastatessa vuotuista sademäärää.

Läpivalutettujen vesien pH-arvot nousivat huuhtelun edistyessä selvästi 1,3—2,0 pH-yksikköä, lukuunottamatta hiekkamaata, missä suodoksen pH pysyi samana. Kalsiumia, magnesiumia, kaliumia, natriumia, sinkkiä ja rikkiä huuhtoutui runsaimmin 5—7 ensimmäisellä huuhtelukerralla, jonka jälkeen huuhtoutuneet ainemäärät vähenivät ja tasaantuivat.

Happamin, pH 3,5:n huuhteluvesi uutti eri huuhtelukerroilla eniten kalsiumia ja magnesiumia kaikista maalajeista, kaliumia vain hiekasta ja natriumia savesta. Magnesiumin kokonaishuuhtoutuma oli suurin happamimmalla huuhteluvedellä kaikista maalajeista, kalsiumin hiekasta ja saves-

ta, kaliumin hiekasta ja hiesusta, sekä natriumin ja boorin savesta. Sensijaan alumiinin kokonaishuuhtoutuma oli pienin happamimmalla huuhtelulla hiekkamaata lukuunottamatta, jossa eroa ei ollut. Samoin raudan huuhtoutuma oli savesta happamimmalla nesteellä pienin. Fosforin, mangaanin, kuparin ja sinkin huuhtoutumisessa ei selviä suuntaa osoittavia eroja hapanvesihuuhtelujen välillä voitu todeta.

Huuhtelun jälkeen maasta mitattujen helppoliukoisten ravinteiden pitoisuuksissa ei todettu mitään eroja eri hapanvesikäsittelyjen välillä, ei myöskään maiden pH-arvoissa eikä vaihtuvissa kationeissa ollut eroja.

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 345—358 (1991)

Seria AGROGEOLOGIA ET -CHIMICA N. 162 — Sarja MAA JA LANNOITUS n:o 162

# EFFECT OF CLAY SOIL STRENGTH AND STRUCTURE ON ROOT PENETRATION AND CROP YIELD

LIISA PIETOLA

PIETOLA, L. 1991. **Effect of clay soil strength and structure on root penetration and crop yield.** Ann. Agric. Fenn. 30: 345—358. (Agric. Res. Centre of Finland, Inst. Crop and Soil Sci., SF-31600 Jokioinen.)

The influence of soil mechanical impedance on the root growth and yield of sugar beet (*Beta vulgaris* L.) and maize (*Zea mays* L.) was studied on a clay soil in 1985. In the studies on crop production, spring wheat (*Triticum aestivum* L.) was used as the control. The experimental plots were compacted by tractor wheels (with 3000 kg axle-load and 120 kPa ground pressure) 0, 1, 2, or 4 times before seed bed preparation. Alterations in soil physical characteristics caused by compaction were measured.

Mechanical impedance clearly affected root growth. Sugar beet root was able to make use of naturally occurring soil pore spaces and penetrated the compacted soil on an average of 20° from the vertical axis, as compared to 15° in uncompacted soil. The growth of the thicker maize seminal root was more horizontal than vertical. When soil strength increased near the growing root, maize seminal root deflected more than beet root. Deflection of sugar beet ($r = 0.38^{***}$) and maize ($r = 0.47^{***}$) roots depended on the difference in the soil strengths of two superimposed soil layers. Crop production was not affected significantly by wheel traffic, which was not severe due to the unusual drought in early spring.

Index words: soil compaction, mechanical impedance, soil structure, root penetration, sugar beet, maize, wheat.

## INTRODUCTION

Soil strength can be an important limiting growth factor in compacted soils. As POHJANHEIMO and HEINONEN (1960) have shown with barley, the hardening and drying out of clay loam soil may entirely inhibit the penetration of roots into the subsoil. Soil resists the local deformation caused by roots, and there is a definite upper limit to the pressure which can be exerted by roots of a given species. In artificial conditions, this maximum root growth pressure of young seedling tap roots has been presented to lie near 1 000 kPa (TAYLOR and RATLIFF 1969, EAVIS et al. 1969).

Soil structure plays a significant role in governing the stress reactions of soil strength on root growth. A clay soil of heterogenous structure has channels with no physical restraint, but also surfaces of high mechanical impedance. Root penetration can be limited by the buckling of roots, when the root grows across a macro pore and meets a solid surface (DEXTER and HEWITT 1978). The density of

large pores has a great influence on root penetration, because, as demonstrated clearly by WIERSUM (1957), in a rigid system the root is only able to penetrate a pore which has a diameter exceeding that of the young root. This is well in agreement with WIKLERT (1960), who studied the development of roots in cereals and turnip rape and showed, that in clay soil below the depth of cultivation, roots grew only in channels and hollow spaces.

The field experiment reported here was carried out to study the root penetration of sugar beet and maize on a clay soil of heterogenous structure. The significance of wheel traffic on clay soil strength and structure, and finally, on crop production was studied as well. Main attention was drawn to the difference in penetrometer resistance of two superimposed soil layers and its influence on the deflection of sugar beet root and maize seminal root. The morphological deformities caused by soil mechanical impedance shown by other plant species, such as diameter growth (ABDALLA et al. 1969) and compensatory growth of laterals (e.g. WIKLERT 1960, VOORHEES et al. 1975) were studied as well.

## MATERIAL AND METHODS

### Treatments

The field experiment was laid out in Jokioinen (60°49′ N, 23°28′ E) during the growing season 1985, and set up according to the method of split-plot design with four replicates. Three different plant species were used in the main plots, which were divided to four sub-plots (3 m × 15 m), according to the compacting of leveled, ploughed soil before spring tillage:

A. Plant species
$A_1$ = sugar beet
$A_2$ = maize
$A_3$ = spring wheat

B. Soil compaction

$B_0$ = no traffic by the tractor
$B_1$ = once, with a single wheeled tractor
$B_2$ = twice, »
$B_4$ = four times, »

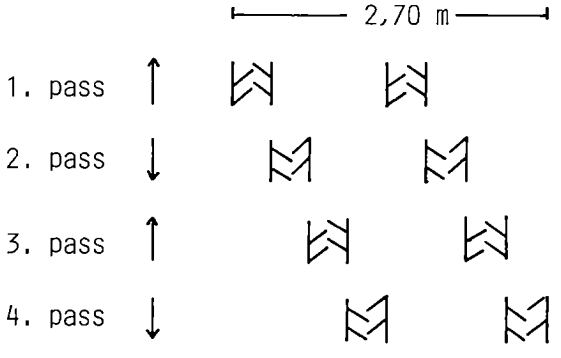


Fig. 1. Principle of compaction treatment $B_1$, where whole surface area of one sub-plot is compacted once by tractor wheels.

In the treatment of $B_1$, the sub-plot was compacted by driving four times over the plot according to the principle in Fig. 1. The rear axle load of the tractor was 3 000 kg with a ground pressure of 120 kPa, as calculated by the method of Inns and Kilgour (SOANE et al. 1980).

After compacting treatments, the 18th of May, spring tillage and placement fertilization (N 130, P 55, K 105, B 1 kg per hectare) were carried out over the whole field, perpendicular to sowing direction with a double wheeled tractor. The field was harrowed four times to the depth of 5—7 cm. Sugar beet seeds were sown 3 cm deep at a row distance of 45 cm, and maize was sown approximately 5 cm deep

at a row distance of 50 cm. Wheat was sown to a depth of about 5 cm. Later, sugar beets were spaced out to a plant distance of 25 cm and maize to 15 cm.

Two weeks after sowing, the mechanical impedance in each sub-plot profile was measured by a cone penetrometer (ANDERSON et al. 1980) to the depth of 52 cm at 3.5 cm intervals. The kilograms shown by the penetrometer were converted into bars with the coefficient 0.762, as the diameter of cone was 12.9 mm (ANON. 1979). The resistance in the profile of each sub-plot was measured eight times, from which the medians were calculated.

Wheat was harvested 112, maize 122, and sugar beet 142 days after sowing. Maize was harvested as silage. The harvesting area was 34 $m^2$ for wheat, 18 $m^2$ for maize, and 24 row meters for sugar beet. The sum of the gaps over 50 cm in the sugar beet rows was subtracted from 24 m before calculating the yields per hectare.

## Experimental soil and weather conditions

The top soil (0—20 cm) contained on average of a 45 per cent clay fraction (<2 μm) and 2.9 per cent organic carbon. Nutrient contents were fairly good. Clay content in the subsoil (20—40 cm) was higher (54 per cent clay fraction and 0.9 per cent organic carbon).

In May, June and July, the mean day temperatures were lower in 1985 than the long-term averages (Table 1). This factor, in addition to a cloddy seed bed, retarded the emergence of maize and sugar beet. August was very warm and rainy, and thus the conditions favoured the growth of these crops.

## Soil samples

For soil moisture gravimetric analysis (105 °C) on the compacting date, soil samples were taken from $B_0$-plots by a soil core sampler (HEINONEN 1960) at 2.5 cm intervals to a depth of 0—20 cm and at 5 cm intervals to a depth of 20—40 cm.

In autumn, soil samples for porosity measurements were collected from each $B_0$- and $B_4$-plots with two replicates. Samples in metal cylinders, 200 $cm^3$ by volume, were taken from the layers of 0—10, 10—20, 20—30 and 30—40 cm. Soil moisture at the suction of field capacity (10 kPa) was determined by the method described by AURA (1983). Moisture at the suction of wilting point (1 500 kPa) was determined in the core layer, about 40 $cm^3$ by volume, in one replicate. Soil density was determined by the pyknometer method for the calculation of total air space. The pore diameter corresponding to the water potential was calculated on the basis of the capillary-rise formula.

Table 1. Weather conditions at Jokioinen in 1985 and the 30-year average.

| | Mean day temperature °C | | Precipitation mm | |
|---|---|---|---|---|
| | 1985 | 1931—1960 | 1985 | 1931—1960 |
| May | 8.6 | 8.8 | 43 | 39 |
| June | 13.2 | 13.7 | 41 | 42 |
| July | 15.3 | 16.2 | 55 | 70 |
| August | 15.5 | 14.7 | 119 | 74 |
| September | 8.9 | 9.7 | 51 | 61 |
| | $\bar{x}$ 12.3 | 12.6 | Σ 309 | 286 |

## Measurements of root penetration

During a seven-week period in June—July, the growth of 52 sugar beet roots and 52 maize seminal axes was studied in excavated pits by measuring both the growing direction and soil strength of the soil profile in $B_0$- and $B_4$-plots. There was a special sampling area at the end of each plot for root studies and soil sampling. The soil was removed gradually to expose the root. The depth of the seed was measured, and at this depth the first measurement of soil strength was determined in the immediate vicinity of the root by a pocket penetrometer (h = 15 cm) with a needle diameter of 1 mm (Fig. 2).

This pocket penetrometer was used as guide to measure penetration resistance of roots. It was compiled by M. Cosse, 41 Boulevard de la Vilette, 75010 Paris, and used also by the Station of Soil Science in Avignon. Pressure recorded as grams could not be transformed to pressure units, because no coefficient for this

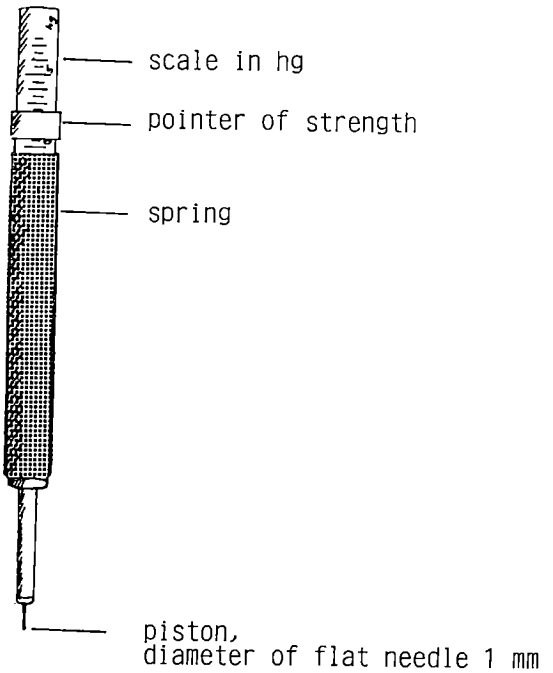


Fig. 2. Pocket penetrometer of flat needle (Ø = 1 mm).

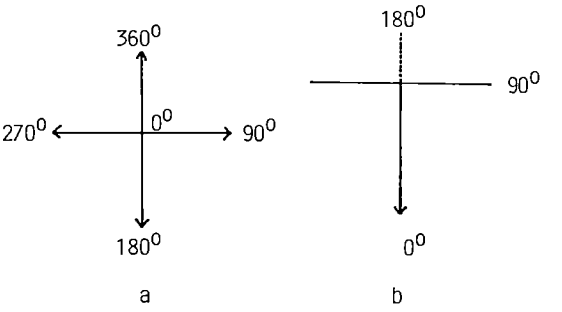


Fig. 3. Degrees of the growth direction in plant roots. Direction on the horizontal plane = a, deviation from vertical direction = b.

penetrometer was available. A flat needle has a large effective diameter (WHITELEY and DEXTER 1981) under clay soil conditions, and this effective diameter could not be determined in this study.

At the depth of the penetrometer measurement, the direction of root growth was measured in degrees with a protractor. Growth direction was recorded with two values; as direction on the horizontal plane, and as deviation from the vertical axis (Fig. 3). For example, if the root grew downwards, the direction was recorded with the notation 0/0. Note 270/90 showed that the root grew to the left horizontally.

The penetrometer resistance of soil (as the median of 3—4 measurements) and growth direction of the root were determined at 1 cm intervals in depth. If the root grew abnormally with strong diametric growth or buckling, more measurements were recorded. The last penetrometer pricks of one profile were carried out from the side of the root apex. After loosening the whole plant from the soil, samples for moisture and bulk density determination were taken by a soil core sampler (HEINONEN 1960) to the depth of the root apex, from two places in close proximity to the excavation.

The results of soil penetrometer resistance and root growth direction were recorded on graph paper, where the root was also drawn

with two dimensions, including abnormal laterals or deformities. Soil heterogeneity, due to cracks, earthworm holes, straw and stones, caused difficulties in measurement, and therefore all these disturbances were recorded on the graph papers. Each root was dried in a press in the growing position according to the measurements of growth direction and the drawing.

### Statistical analyses

The results were studied statistically employing the analysis of variance and Tukey's tests HSD (Honestly Significant Difference) to find significant ($P = 0.05$) differences between means. Soil parameters and yields of each plant species were studied according to randomized complete-block design, where wheel traffic represented the treatments.

As the results of the soil moisture and bulk density determinations represented the soil layer of 2.5 cm (HEINONEN 1960), several penetrometer resistances were determined in this layer. Thus, the same moisture and bulk density were recorded together with all separate penetrometer resistances measured in this one layer, when analysing the dependences between these soil parameters. In the analysis of variance, these soil parameters were classified according to soil depth at 5 cm intervals.

The linear correlations between the parameters measured in the root studies were also determined. The significance of the correlation coefficient (r) at the 0.1 % level was marked ***. The second-degree polynomial regression was used, because it gave a slightly better coefficient of determination ($R^2$) than linear regression. In these studies, the results of both $B_0$- and $B_4$-treatments were combined.

## RESULTS

### Effect of wheel traffic on soil physical characteristics

The moisture status of soil at the compacting date is presented in Fig. 4. The soil was not as moist as usual in spring, and hence the mechanical impedance, as measured by the large cone penetrometer, was not greatly affected by the tractor treatments (Fig. 5). At the depth of 14—24.5 cm, there was a significant ($P = 0.05$) difference between zero and four passes. Between zero and one tractor pass, a significant difference was found at the layer of 21—24.5 cm, and between zero and two passes at the depths of 24.5 cm and 27.5 cm. In comparison with one pass to four passes, the cone penetrometer resistance at the depth of 14 cm increased significantly, but the difference was only 280 kPa. At the depth of 10.5 cm, the difference between two and four passes was 400 kPa ($P = 0.05$).

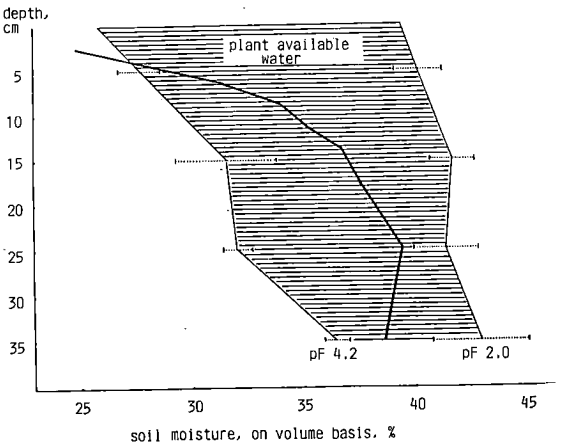


Fig. 4. Soil moisture status on the compacting date.

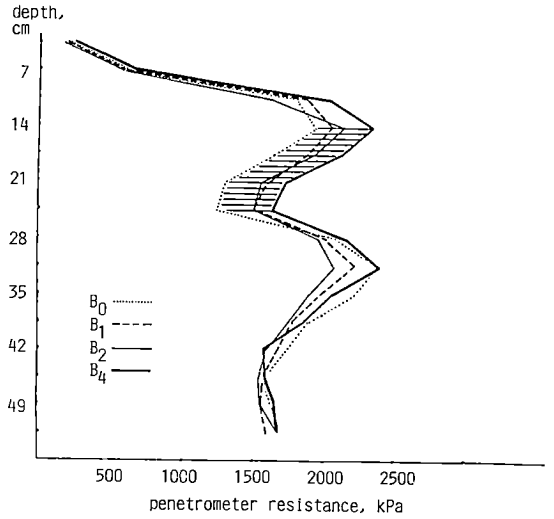


Fig. 5. Effect of wheel traffic on soil mechanical impedance, measured by cone penetrometer (Ø = 12.9 mm). Soil without compaction = $B_0$, compaction of one tractor drive = $B_1$, compaction of two drives = $B_2$ and four drives = $B_4$. Shaded area = significant compaction (P = 0.05).

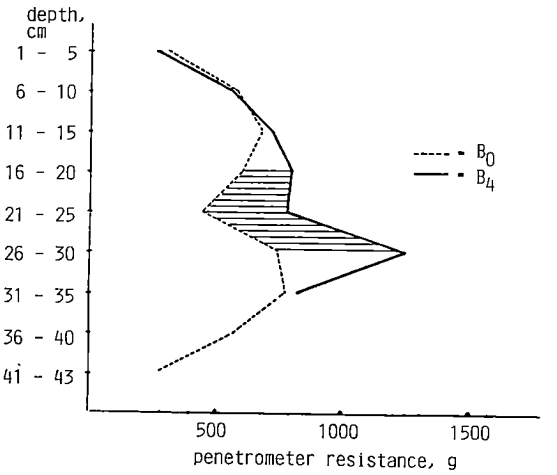


Fig. 6. Effect of compaction on mechanical impedance near roots, measured by pocket penetrometer. Soil without compaction = $B_0$, compaction of four tractor drives = $B_4$. Shaded area = significant compaction (P = 0.05).

The influence of tractor driving on soil porosity was not statistically significant due to very large dispersion (Table 2). Nevertheless, the percentage (by volume) of large pores (ø >30 µm) was higher in uncompacted soil in all layers to a depth of 40 cm, compared with the treatment of four passes. Between these treatments, the difference in total soil porosity at the depth of 10—20 cm was 3.3 percentage units.

Compared with no tractor driving, four tractor passes did not greatly affect the soil bulk density or moisture status. In the samples collected simultaneously with root growth determinations, the increase in soil bulk density at the depth of 21—25 cm was significant (P = 0.05), but its magnitude was only 0.1 g/cm³. By four tractor passes, the soil moisture (on both a dry mass basis and a volume basis) was decreased only about 1 percentage unit (P = 0.05) to the depth of 15 cm. On the contrary, at the depth of 21—25 cm, the moisture content (on a volume basis) was significantly (2.4 percentage units) higher in compacted plots.

## Effect of four tractor passes on root growth

Compared with no tractor driving, the influence of four tractor passes on the soil

Table 2. Effect of soil compaction on pore size distribution. Soil without tractor driving = $B_0$, compaction with four tractor drives = $B_4$.

| Depth, cm | >30 µm | | Volume-% 0.2—30 µm | | <0.2 µm | |
|---|---|---|---|---|---|---|
| | $B_0$ | $B_4$ | $B_0$ | $B_4$ | $B_0$ | $B_4$ |
| 0—10 | 16.3±4.0 | 15.1±5.3 | 10.3±0.2 | 11.5±0.2 | 27.7±1.3 | 28.6±1.6 |
| 10—20 | 11.9±4.1 | 8.8±4.5 | 10.8±2.8 | 9.5±1.7 | 31.6±3.2 | 32.7±2.2 |
| 20—30 | 7.9±3.0 | 6.9±2.9 | 5.8±3.3 | 10.1±1.5 | 32.1±0.9 | 30.9±5.1 |
| 30—40 | 7.0±3.6 | 6.0±1.6 | 7.0±0.1 | 6.2±1.7 | 36.5±0.8 | 34.0±2.7 |

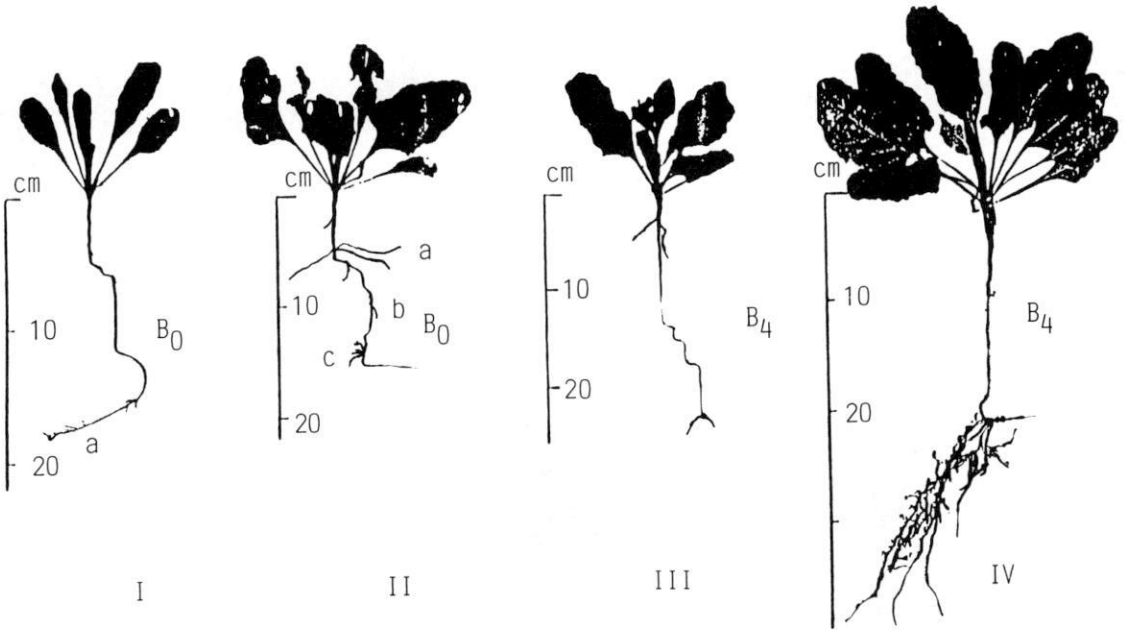


Fig. 7. Effect of compacting on penetration and morphological deformities of sugar beet roots. Soil without compaction = $B_0$, compaction of four tractor drives = $B_4$.

I Root (2.7.1985) deflected under constraint of 1 000—1 200 g and grew vertically in cracks. Branching occurred near root tip under 600—1 000 g (a). Root apex was deformed and thickened by soil strength of 1 400 g.

II Impedance of 1 500 g caused root (11.7.1985) deflection and branching (a). Later, root grew downwards in cracks (b). Under 700—1 000 g, root was developed by compensatory growth of laterals and diameter growth (c). Root apex grew horizontally inside straw with no constraint.

III Root (10.7.1985) grew downwards in cracks, but buckled under constraint of 1 000—1 300 g.

IV Branching of root (17.7.1985) occurred in hollow spaces and cracks after vertical growth under pressure of 700—800 g.

strength on the patterns of root growth is presented in Fig. 6. In compacted plots, this strength measured by the pocket penetrometer, was significantly ($P = 0.05$) higher than in soil with zero passes, at the depth of 16—30 cm.

Compaction did not significantly affect the growth depth of the main roots. During the last sampling week in the middle of July the root tips of sugar beet were found at a depth of approximately 30 cm. Maize seminal roots grew only at a depth of 10—15 cm.

The effect of four tractor passes on growth direction was slight, but significant ($P = 0.05$): sugar beet roots grew on an average of 15° ($n = 379$) from the vertical axis in a soil without compaction, but in compacted soil the deviation was 20° ($n = 401$). Contrary to sugar beet, maize grew in a more downward direction in the plots subjected to tractor driving, but in both treatments the growth was more horizontal than vertical. The deviations from the vertical axis were 60° ($n = 384$) and 67° ($n = 297$) in soil with and without compaction, respectively.

Pictures of a few of the roots dried in the press in their growing positions according to the measurements and drawings, are presented in Figs. 7 and 8. Both sugar beet and maize roots reflected and followed the direction of the least mechanical impedance. Branching now oc-

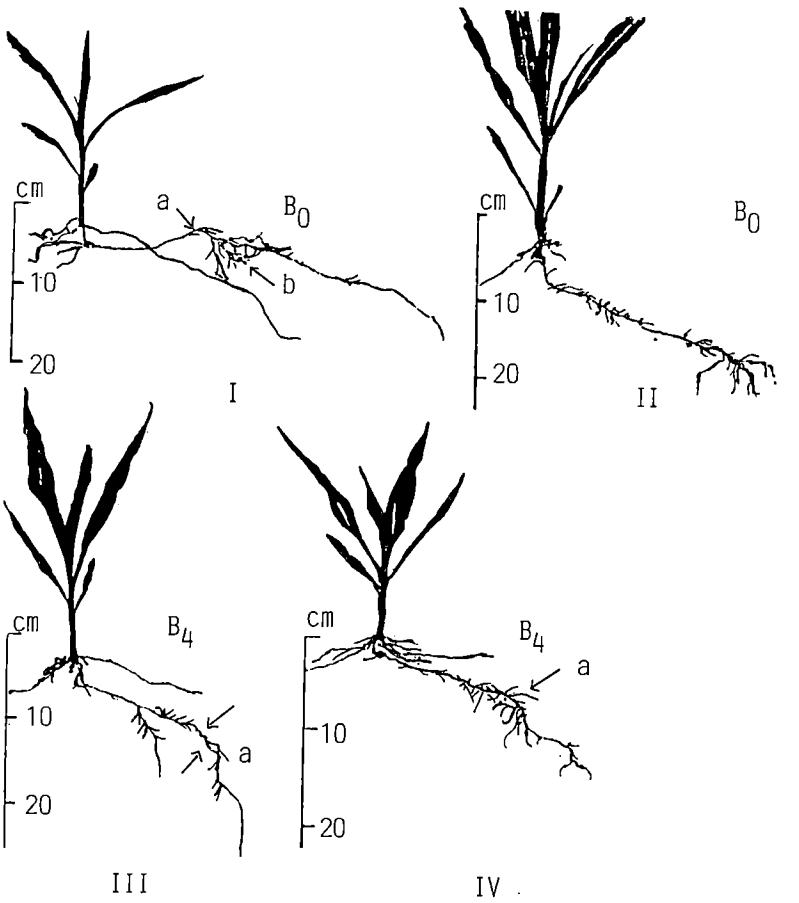


Fig. 8. Effect of compacting on penetration and morphological deformities in maize seminal roots. Soil without compaction = $B_0$, compaction of four tractor drives = $B_4$.

I Root (1.7.1985) grew horizontally even when resistance was 300—800 g, and deflected along ped of strength 150—500 g (a). Later root branched in 200 g (b). Root apex grew almost vertically in the crack.

II Typical root profile (15.7.1985), where root deflected under resistance of 600—1 100 g with compensatory growth of laterals and finally branched in the cavity.

III Root (8.7.1985) deflected and followed soil canals (a). Arrows show abnormal diameter growth, caused by pressure of 1 400 g. Root apex developed in the crack.

IV Branching occurred under constraint of 500—1 300 g (a) and the root (8.7.1985) turned downwards at a resistance of 500 g. Root apex was 1.5—2 times as thick as normal and deflected under penetrometer resistance of 1 300 g.

curred in hollow spaces and cavities if growth had been prevented earlier. In the absence of large pores or cracks the root was thickened by constraint. These symptoms of high soil strength were observed in the plots which had been compacted, as well as in the soil with no tractor passes.

## Dependences between soil physical properties and root growth

The pocket penetrometer resistance in the patterns of root growth was not closely dependent on the soil bulk density ($r = 0.18^{***}$). In addition, soil moisture (on a dry mass basis) had a

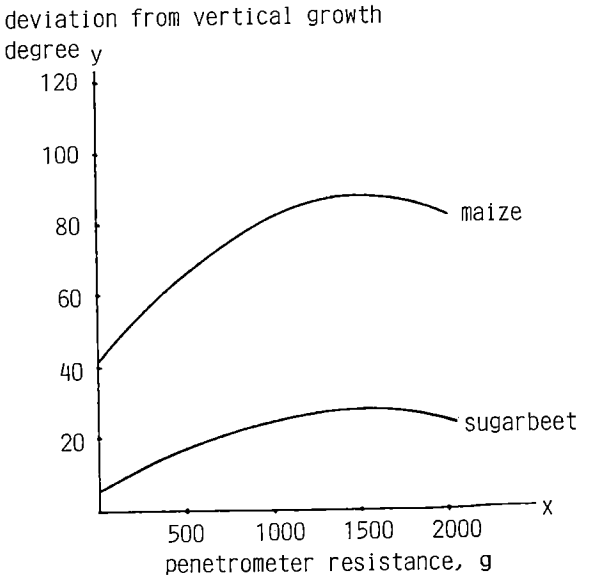


Fig. 9. Relationship between pocket penetrometer resistance near roots (x) and growth direction of vertical plane (y) for sugar beet $y = 4.9 + 0.03x - 1 \times 10^{-5}x^2$ ($R^2 = 0.070$) and for maize $y = 42 + 0.06x - 2 \times 10^{-5}x^2$ ($R^2 = 0.107$).

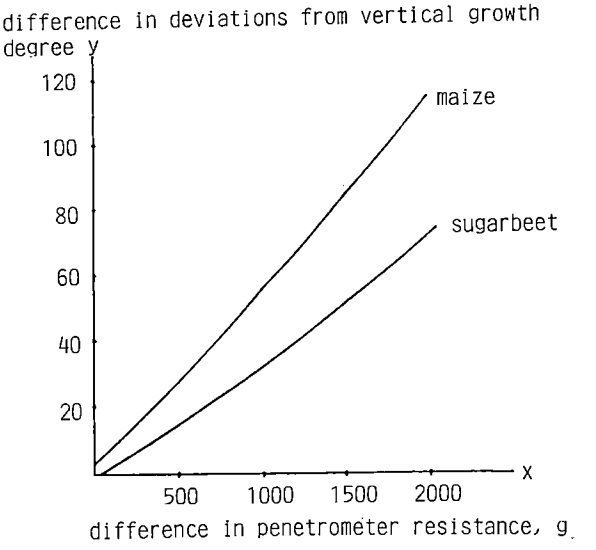


Fig. 10. Relationship between pocket penetrometer resistance near roots (x) and growth direction on vertical plane (y), when differences of these parameters ($x_n - x_{n+1}$; $y_n - y_{n+1}$) were used in sequence regarding soil depth (n) for sugar beet $y_n - y_{n+1} = -0.9 + 0.03\,(x_n - x_{n+1}) + 3 \times 10^{-5}\,(x_n - x_{n+1})^2$ ($R^2 = 0.145$) and for maize $y_n - y_{n+1} = 2.2 + 0.05\,(x_n - x_{n+1}) + 3 \times 10^{-6}\,(x_n - x_{n+1})^2$ ($R^2 = 0.226$).

very slightly negative dependence on this resistance ($r = 0.12^{***}$). No reliable correlation was found between soil moisture (on a volume basis) and pocket penetrometer resistance. On average, at the depth of 0—20 cm soil moisture was 31—33 % on a bulk basis during the sampling period. The third week was moister, and thus the measurements for this week were not used in the correlation analysis to prevent errors in soil strength, caused by differences in soil moisture status.

The deviations from vertical growth axis (y) in both sugar beet ($r = 0.251^{***}$) and maize ($r = 0.297^{***}$) were only slightly dependent on the penetrometer resistance (x) near the roots. The regression equation (Fig. 9) for sugar beet was $y = 4.9 + 0.03x - 1 \times 10^{-5}x^2$ ($R^2 = 0.070$) and for maize $y = 42 + 0.06x - 2 \times 10^{-5}x^2$ ($R^2 = 0.107$). When differences of pocket penetrometer resistance ($x_n - x_{n+1}$) and growth direction as deviation from vertical direction ($y_n - y_{n+1}$) in two superimposed soil layers (n, n + 1) were

Table 3. Effect of soil compaction on crop production. Soil without tractor driving = $B_0$, one drive = $B_1$, two drives = $B_2$, four drives = $B_4$.

| Plant | kg/ha | | | |
|---|---|---|---|---|
| | $B_0$ | $B_1$ | $B_2$ | $B_4$ |
| Sugarbeet | 30 400 ± 1 100 | 33 400 ± 1 000 | 29 900 ± 400 | 29 500 ± 1 000 |
| Silage maize (D.M.) | 4 580 ± 170 | 4 440 ± 130 | 4 750 ± 360 | 4 460 ± 320 |
| Spring wheat (moisture 15 %) | 4 470 ± 140 | 4 470 ± 180 | 4 570 ± 140 | 4 650 ± 60 |

used as variables in regression analyse, the correlation was closer; in sugar beet r was 0.380*** and in maize 0.474***. The regression equation (Fig. 10) for sugar beet was $y_n - y_{n+1} = -0.9 + 0.03(x_n - x_{n+1}) + 3 \times 10^{-5}(x_n - x_{n+1})^2$ ($R^2 = 0.145$) and for maize $y_n - y_{n+1} = 2.2 + 0.05(x_n - x_{n+1}) + 3 \times 10^{-6}(x_n - x_{n+1})^2$ ($R^2 = 0.226$).

### Effect of wheel traffic on crop production

The yields of three plant species in different compacting treatments are shown in Table 3. Tractor traffic did not affect the yields of silage maize or wheat, but one tractor pass significantly increased (P = 0.05) the production of sugar beets, compared with all the other treatments.

## DISCUSSION

### Effect of wheel traffic on soil porosity and penetrability

In agreement with AURA (1983), the effect of soil compaction by a 3 000 kg tractor in spring was found at the depth of 15—25 cm. The experimental soil profile had, however, high penetrometer resistance and low volume of large pores even without compaction. In addition, the moisture status of soil during the compaction process was rather low in spring 1985. Thus, the effect of traffic must have been mostly elastic. Therefore it did not significantly affect (P = 0.05) soil porosity. The volume of large pores (0 > 30 µm) decreased on average only 3 percentage units at the depth of 10—20 cm by four tractor passes. This was less than AURA (1983) reported.

In many soil conditions, small penetrometers must exert a relatively greater pressure to penetrate soil than large penetrometers. This is due to an effective diameter of a penetrometer which is larger than the true diameter (WHITELEY and DEXTER 1981 b). Moreover, penetration pressures depend on probe geometry (VOORHEES et al. 1975), and basically a probe moving into a soil shows more soil resistance to the probe than to a root (STOLZY and BARLEY 1968, WHITELEY et al. 1981). At best, resistances measured by penetrometers should be regarded as comparative, not absolute values.

Thus in the present study, the measurements of soil resistance by cone penetrometer and by the flat needle of a pocket penetrometer are not absolutely comparable, even if the measurements of the pocket penetrometer could be transformed into pressure units. Consequently, the penetrometer measurements cannot show if soil strength was different near the roots compared with the overall soil profile as measured by the cone penetrometer. However, soil strength near the roots increased 200—500 g at the depth of 15—30 cm. This direction was recorded by the cone penetrometer as well, i.e. an increase of 400—500 kPa at the depth of 15—25 cm by four tractor drives.

### Effect of soil strength and structure on root growth

The results of other studies under field conditions (VOORHEES 1976, 1980) indicate the high susceptibility of both sugar beet and maize roots to soil compaction. In the present study, the growing depths were measured only in June—July, and during this period, the depths of both sugar beet and maize were not affected by wheel traffic. Considering the high penetrometer resistance and heterogeneity of the soil in all of the treatments, this result is understandable.

Concerning the direction of root growth, there were small yet statistical significant differ-

ences between the treatments with zero and four tractor passes. In compacted soil, sugar beet root grew 5° more horisontally than in soil without wheel traffic, when the growing direction was 15°. To the contrary, the maize root growing direction of 67° unexpectedly decreased to 60° by four tractor drives. Thus, it deviated much more from vertical growth than beet root. Since the seminal roots of maize are of a larger diameter than those of the sugar beet root, it is obvious that they are less able to make use of naturally-occurring soil pore spaces.

This finding is in agreement with AUBERTIN and KARDOS (1965), who found under controlled conditions maize roots to grow in approximately the same way in all nonrigid bead systems, regardless of the size of the pores. Moreover, in a rigid system, any reduction in pore diameter below 412 µm resulted in a reduction in root growth. Thus maize roots, including seminal roots, do not grow downwards through existing pore space as the sugar beet roots do, but mainly extend through the soil due to their ability to displace the soil particles and create their own path through the soil.

Soil strength caused an increase in root diameter, which was accompanied by lateral root growth. This occurred when the soil had pores where laterals of smaller diameter could enter freely and from which axes were excluded. This agrees with the studies of other plant species, e.g. those by WIKLERT (1960), VOORHEES et al. (1975). If compensatory growth of laterals was repressed, strong branching took place later in the hollow space. Visual observations showed that maize seminal root was more susceptible to clay soil strength than sugar beet root; maize seminal root deflected and branched under a resistance of around 400 g, whereas the morphological deformaties of sugar beet root became obvious under a constraint of 1 000 g on average.

### Dependences between soil strength and root deflection

It is well known that soil penetrometer resistance increases with increasing soil moisture tension (TAYLOR and GARDNER 1963). Due to the similar moisture status in the experimental soil during the sampling period, the soil strength measured by the pocket penetrometer near the roots was, however, very slightly correlated to soil moisture. There was no dependence between soil strength and bulk density. This indicates heterogeneity in the experimental soil, shown also by EHLERS et al. (1983).

In spite of the similar moisture conditions, and numerous measurements which allowed very significant correlation coefficients, the positive correlation between pocket penetrometer resistance and root deflection was not close. Soil heterogeneity was a noteworthy reason for this poor correlation; the ability of the root apex to grow along planes of weakness reduces the soil strength encountered by it as compared with a rigid penetrometer probe. Because maize seminal root had a weaker ability to grow in narrow cracks, it had better relationships between soil strength and root deflection than sugar beet root. Moreover, under field conditions soil physical growth factors cannot be separated, and the problem is complicated by interactions between compaction and aeration (VOORHEES et al. 1975). Nutrition has significant influences on the elastic behaviour of roots as well (WHITELEY and DEXTER 1981 a).

The difficulties of soil strength measurement by a penetrometer near the roots were also shown in the regression analysis; the coefficients of determination were low. Moreover, the form of the regression curves of roots (Fig. 9) indicates, that as resistance was over 1 500 g, roots grew more vertically than under this constraint. This is explained by the hypothesis that a penetrometer with a needle diameter of 1 mm could not track the narrow cracks

where penetration in very compacted soil must have occurred.

The buckling and deflection of roots do not associate only with the resistance near the growing root apex. DEXTER and HEWITT (1978) reported that root penetration depends also on the strength of the media from which the root grows. The present study, as well, showed that **if a root passes through the compacted layer it penetrates the next media more easily than a root coming from a loose layer.** The greater the differences in soil penetrometer resistances of two superimposed soil layers, the more powerful was also deflection, as measured by difference of deviations from the vertical growth direction.

A closer relationship existed between the soil penetrometer resistance and the direction of root growth if they are expressed by differences in the parameters of two superimposed soil layers, rather than between the parameters of one media. Essentially, this shows that soil structure has a contributory effect on the stress reactions caused by soil strength. Nevertheless, under field conditions, it is difficult to reach quantitative conclusions with respect to the significance of such an individual factor as soil strength.

### Productivity of heterogenous compacted soil

One tractor pass increased significantly ($P = 0.05$) the yield of sugar beet, from 30 400 kg/ha to 33 400 kg/ha, by crushing the cloddy seedbed. The beet production did not suffer significantly from soil strength, probably partly due to the very rainy August when even restricted roots had access to enough water. This indicates that soil strength in compacted field will not by itself reduce the productivity of even a crop having a tap root system, providing an adequate and continuing supply of nutrients and water is available in the restricted rooting zone. Even a very restricted root system can take nutrients normally (GOSS 1977). Unfortunately, this study cannot show, if clay soil with minor mechanical impedance would produce, under similar circumstances, higher yields than reported here. Consequently this report cannot agree with ERJALA (1986), that sugar beet production is very susceptible to wheel traffic.

In sandy soil under artificial conditions, STIBBE and TERPSTRA (1981) found that during early growth the dry matter yield of silage maize linearly decreased with increasing penetration resistance of 200 to 1 700 kPa. Corn yields, on the contrary, increase from inter-row compaction, probably due to increased phosphorus uptake (VOORHEES 1980). In the present study the slight compaction was not better than the other treatments. If the production of silage maize is as susceptible to soil mechanical impedance under field conditions as the results of STIBBE and TERPSTRA (1981) indicate, soil heterogeneity must be the reason why an increase of 450 kPa in soil strength could not decrease the dry matter production of 4 500 kg/ha.

According to AGRAWAL (1976), wheat, like cereals in general, is considered to be more resistant to compaction than crops having a tap root system. In fact, soil needs some compaction for optimal cereal production (HÅKANSSON 1986). However, clay soil compaction by a 3 000 kg axle-load with three repetitions can be severe enough to decrease the production of spring wheat yield by 20—30 % as indicated in an earlier Finnish experiment (ELONEN 1980). In this study, even four repetitions had no effect on the crop yield of 4 500 kg/ha. This was due to the unusual drought during the compaction, when comparing the soil moisture status with the results of ELONEN (1980).

*Acknowledgements* — I wish to thank M.Sc. Jyrki Pitkänen, Mr. Risto Seppälä and Mr. Lauri Säisä for their patient measurements of soil strength and growing direction of roots.

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*Manuscript received May 1990*



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SELOSTUS

# Savimaan mekaaninen vastus ja sen vaikutus kasvutekijänä erityisesti juuren kehitykseen

LIISA PIETOLA

Maatalouden tutkimuskeskus

Maan mekaanisen vastuksen vaikutusta sokerijuurikkaan ja maissin kasvuun tutkittiin Jokioisissa hiesusavimaalla. Tutkimusta varten perustettiin kesällä 1985 kenttäkoe, jossa osa koeruuduista tiivistettiin traktorin renkailla kylvömuokkauksen yhteydessä. Maa oli tuona keväänä luontaisesti jo niin liettynyttä ja tiivistä, että kuivahtaneen saven lisätiivistäminen neljästi 3 000 kg:n akselikuormitusta ja 120 kPa:n pintapainetta käyttäen lisäsi maan mekaanista vastusta vain 450 kPa 15—25 cm syvyydessä. Tiivistyskäsittelyt eivät siten aiheuttaneet huomattavia muutoksia sokerijuurikkaan ja maissin juurien kasvuympäristöön eikä kasvutapaan. Tämä heijastui myös sadonmuodostukseen; tiivistyskäsittelyt eivät johtaneet sanottaviin eroihin sokerijuurikkaan, maissin eikä verranteena olleen vehnän sadoissa.

Tiiviin heterogeenisen savimaan juuritutkimukset osoittivat, että sokerijuurikkaan juuri seuraa pienimmän mekaanisen vastuksen kohtia maassa ja ohuen juurenkärkensä avulla kasvaa pienissä maan halkeamissa alaspäin. Maissin paksuhko siemenjuuri kasvoi sitä vastoin vinosti. Kasvien välinen ero juurten kasvusuunnissa oli keskimäärin 45°.

Juurten taipumisella ja maan mekaanisella vastuksella juuren välittömässä läheisyydessä oli selvä riippuvuus: mitä suurempi oli mekaanisen vastuksen ero pienellä taskupenetrometrillä mitattuna juuren kasvaessa maakerroksesta toiseen, sitä voimakkaampi oli juuren taipuminen tai suoristuminen (sokerijuurikkaan $r = 0.38^{***}$, maissin $r = 0.47^{***}$). Taipumisen lisäksi juuri paksuuntui ja/tai haaroittui, jos juurta ympäröivässä maassa oli juuren haaroille kasvutilaa, tai juuren löydettyä suuremman raon tai onkalon. Tällöin juuri ikään kuin purki puristuksessa olleen kasvupaineensa täyttämällä koko onkalon joskus hyvin paksuilla ja haurailla juurenhaaroilla.

Tutkimus osoitti, että varsinkin sokerijuurikkaan pääjuurella, mutta myös jossain määrin maissin siemenjuurella on kyky käyttää hyväksi maan suuret huokoset, halkeamat ja lieronreiät, mikä vähentää tiiviin, mutta heterogeenisen savimaan mekaanisen vastuksen haitallisuutta.

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 359—373 (1991)
Seria AGROGEOLOGIA ET -CHIMICA N. 163 — Sarja MAA JA LANNOITUS n:o 163

# SPRINKLER IRRIGATION OF FIELD CROPS DURING RAINY GROWING SEASONS

LIISA PIETOLA and PAAVO ELONEN

PIETOLA, L. & ELONEN, P. 1990. **Sprinkler irrigation of field crops during rainy growing seasons.** Ann. Agric. Fenn. 30: 359—373. (Agric. Res. Centre of Finland, Inst. Crop and Soil Sci., SF-31600 Jokioinen, Finland.)

The investigation was carried out during a six-year period, during which irrigation treatments were followed by heavy rainfall almost every year. The effect of repeated applications of water (3 times approx 30 mm) or one application (on the 1st, 2nd or 3rd date) on eight different crops were studied on a clay soil.

Broad bean profited the most from the excess water. Each year, the yield was increased by one application of water, and only once (1983) did a treatment of three irrigations have an adverse effect on productivity. The higher the yield increased, the better was the quality, i.e. 1 000 seed weight and protein content. On the contrary, pea was very sensitive to the extra moisture. It benefited from one application of water around midsummer in 1980 and 1985, but three applications proved deleterious to both yield production and quality every year of the study.

The spring oilseed rape species were also sensitive to wet clay soil conditions. Their yield was decreased by three irrigations, and one application was either harmful or neutral. The irrigations increased oil content and decreased protein content.

In the early summer, spring cereals utilized more water than the rapes or legumes. With respect to yield production, spring cereals profited more from the irrigations than rapes or pea did. The capacity of wheat to exploit the extra water was slightly better compared to oat or two- and six-rowed barley.

Index words: irrigation, soil water, broad bean, pea, spring oilseeds, cereals, yield, quality.

## INTRODUCTION

The effects of sprinkler irrigation on the productivity of clay soil have been studied in the Nordic countries since the 1960s. From the beginning, these studies mainly dealt with grass crops (JOHANSSON 1965). The positive results of clay soil irrigation on cereals published in Finland (POHJANHEIMO and HEINONEN 1960, ELONEN et al. 1967 b) led to a more intensive establishment of field experiments to determine the effects of irrigation on cereals grown on this soil type (MYHR and ROGNERUD 1974, JOHANSSON 1976, HAUGE et al. 1981, LINNER 1982).

Relatively few investigations concerning the irrigation of grain legumes (ELONEN 1977) or spring oilseed rapes (ELONEN 1974, LINNER 1981) have been published in Fennoscandia. Thus, in 1980, an investigation of sprinkler irrigation on clay soil was started with the aim of studing these crops more thoroughly with cereals. The effects of both the volume and date

of water application were studied.

The experimental years 1980—84 were unusually rainy. In 1981 and 1984 irrigation was carried out only once due to heavy rainfall. Therefore the main object of the present study was to determine the possible differences in tolerance to excess water among the different plant species.

## MATERIAL AND METHODS

### Treatments

The field experiment was established at Jokioinen (60°49′ N, 23°28′ E) in 1980—1985, and set up according to the method of the split-plot design with five replicates. Irrigation treatments (1st, 2nd, 3rd date, all 3 applications or none) were employed in the main plots, which were divided into sub-plots (2 m × 24 m) according to plant species.

Irrigation was performed at night by rotary sprinklers with a radius of 13 ± 2 m. The amount of water supplied by every sprinkling circle was controlled by plastic flasks eguipped with funnels (ELONEN et al. 1967 a). The water applications are presented in Tables 2—3. The experimental soils endured the irrigation every time without slaking.

The experimental leguminous plants were broad bean (*Vicia faba* cv. Mikko) and pea (*Pisum sativum*, cv. Proco). In 1980, a seed mixture of pea and oat was used instead of broad bean. The crops were cultivated in the same way under identical growing conditions side by side. Placement fertilization was carried out using compound fertilizer with a low nitrogen content (N 60 kg/ha). The other experimental plants received more nitrogen (120 kg/ha).

The cultivars of the other experimental plants were as follows:

Spring oilseed rape (*Brassica napus*)
Regent (1980—81), Topas (1982), Karat (1983—85)
Spring oilseed turnip rape (*Brassica campestris*)
Span (1980), Ante (1981—82), Emma (1983—85)
Spring wheat (*Triticum aestivum*):
Ruso (1980), Luja (1981—85)

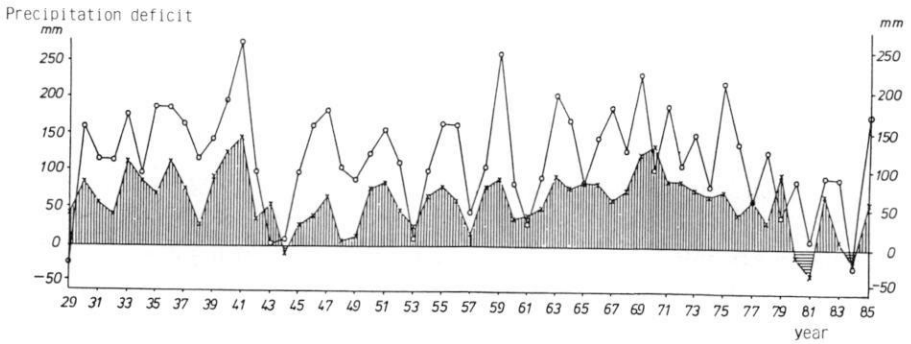



Fig. 1. "Precipitation deficit" as the difference between potential evapotranspiration and precipitation at Jokioinen in 1929—1985 (Ansalehto et al. 1985, data for 1985 provided by Finnish Meteorological Institute)
−x−x (shaded) = deficit in June
−o−o = deficit in May—July

Table 1. Weather conditions at Jokioinen in 1980—1985 and the 30-year average.

| | Mean day temperature °C | | | | | | | Precipitation mm | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 | 1931—60 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 | 1931—60 |
| May | 7.0 | 11.2 | 8.5 | 11.0 | 12.6 | 8.6 | 8.8 | 20 | 19 | 71 | 44 | 66 | 43 | 39 |
| June | 16.4 | 12.8 | 11.2 | 13.3 | 13.1 | 13.2 | 13.7 | 131 | 115 | 25 | 84 | 113 | 41 | 42 |
| July | 16.2 | 16.2 | 16.4 | 16.6 | 14.8 | 15.3 | 16.2 | 36 | 104 | 84 | 41 | 90 | 55 | 70 |
| August | 13.9 | 13.5 | 15.6 | 15.0 | 13.8 | 15.5 | 14.7 | 76 | 88 | 111 | 58 | 69 | 119 | 74 |
| September | 10.5 | 9.5 | 9.7 | 11.0 | 9.2 | 8.9 | 9.7 | 58 | 15 | 67 | 86 | 77 | 51 | 61 |
| | x̄ 12.8 | 12.6 | 12.3 | 13.4 | 12.7 | 12.3 | 12.6 | Σ 321 | 341 | 358 | 313 | 415 | 309 | 286 |

Oat (*Avena sativa*):
Puhti (1980—85)
Barley (*Hordeum vulgare*):
six-rowed: Pomo (1980—84), Arra (1985)
two-rowed: Ingrid (1980—82), Kustaa (1983—85)

## Experimental soil and its moisture conditions

The topsoil (0—20 cm) contained an average of 40 percent of the clay fraction (< 2 µm) and 3.1 percent of organic carbon. Nutrient contents were fairly good. The subsoil (20—40 cm) had a higher clay content (clay content around 50 percent).

In 1980—1985, the growing seasons were abnormally wet, except in 1985. The "precipitation deficit", the difference between potential evapotranspiration and precipitation (VAKKILAINEN 1982) in June or in June—August is presented in Fig. 1, as calculated by the data of ANSALEHTO et al. (1985). Information on mean day temperature and precipitation is given in Table 1.

The moisture condition of the soil during the growing season was studied by the gypsum block method. Immediately after sowing, blocks were dug to a depth of 15 cm, in the treatments with either none or three applications of water. Irrigations were usually carried out when the available water in the topsoil fell below 50 % of the available water capacity. The gypsum blocks registered the soil moisture as available moisture percentages from pF 2 (96 %) to pF 4.2 (5 %) (AURA 1985).

## Analyses of seeds

For the determination of crude protein content in the seeds and grains total nitrogen (analysed to the Kjeldahl procedure using a Tecator apparatus) was multiplied by 6.25, or for wheat by 5.7. The oil content of the rape seeds was

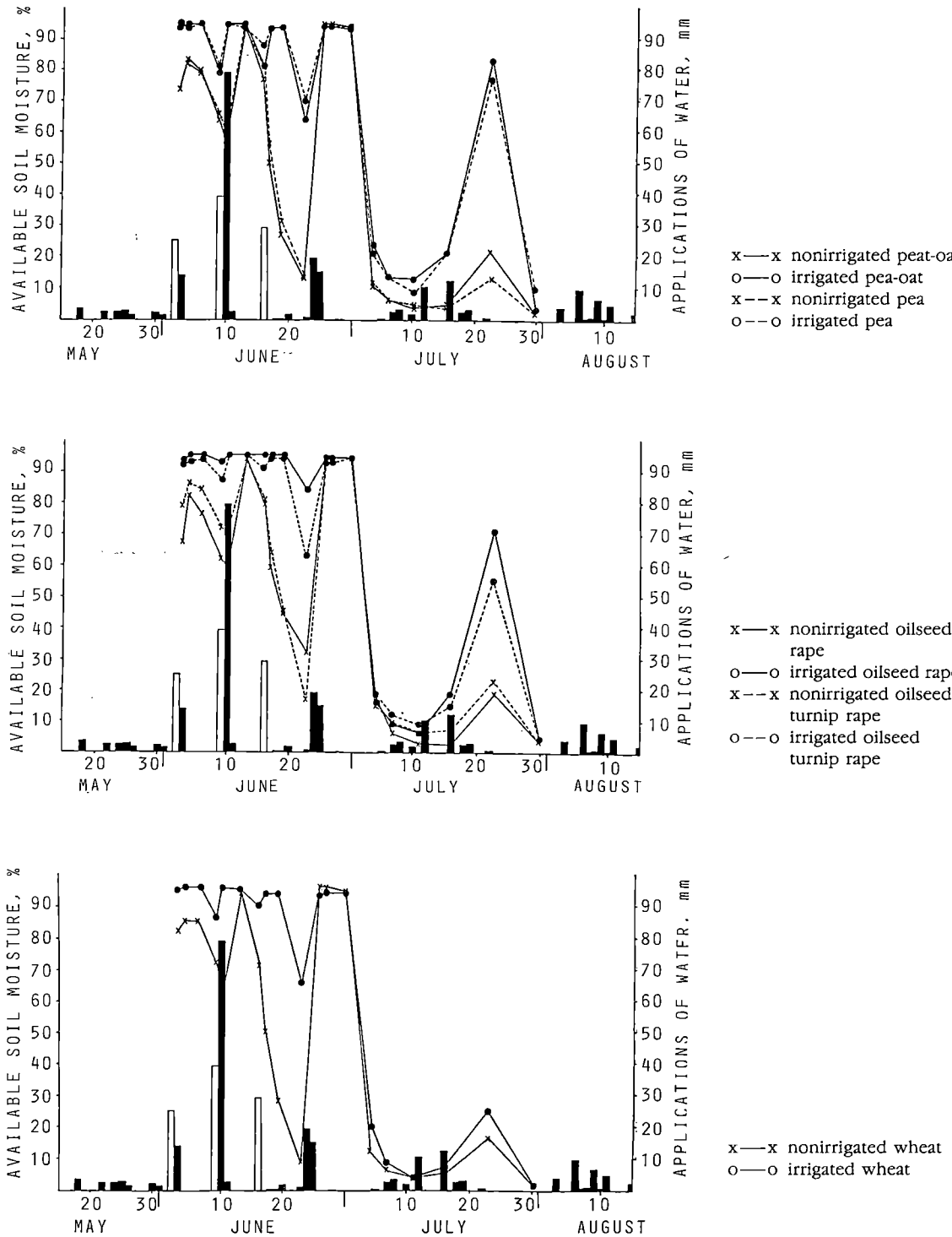



Fig. 2. Soil available water at depth of 15 cm during the 1980 growing season. Black columns show precipitation and white columns irrigations.

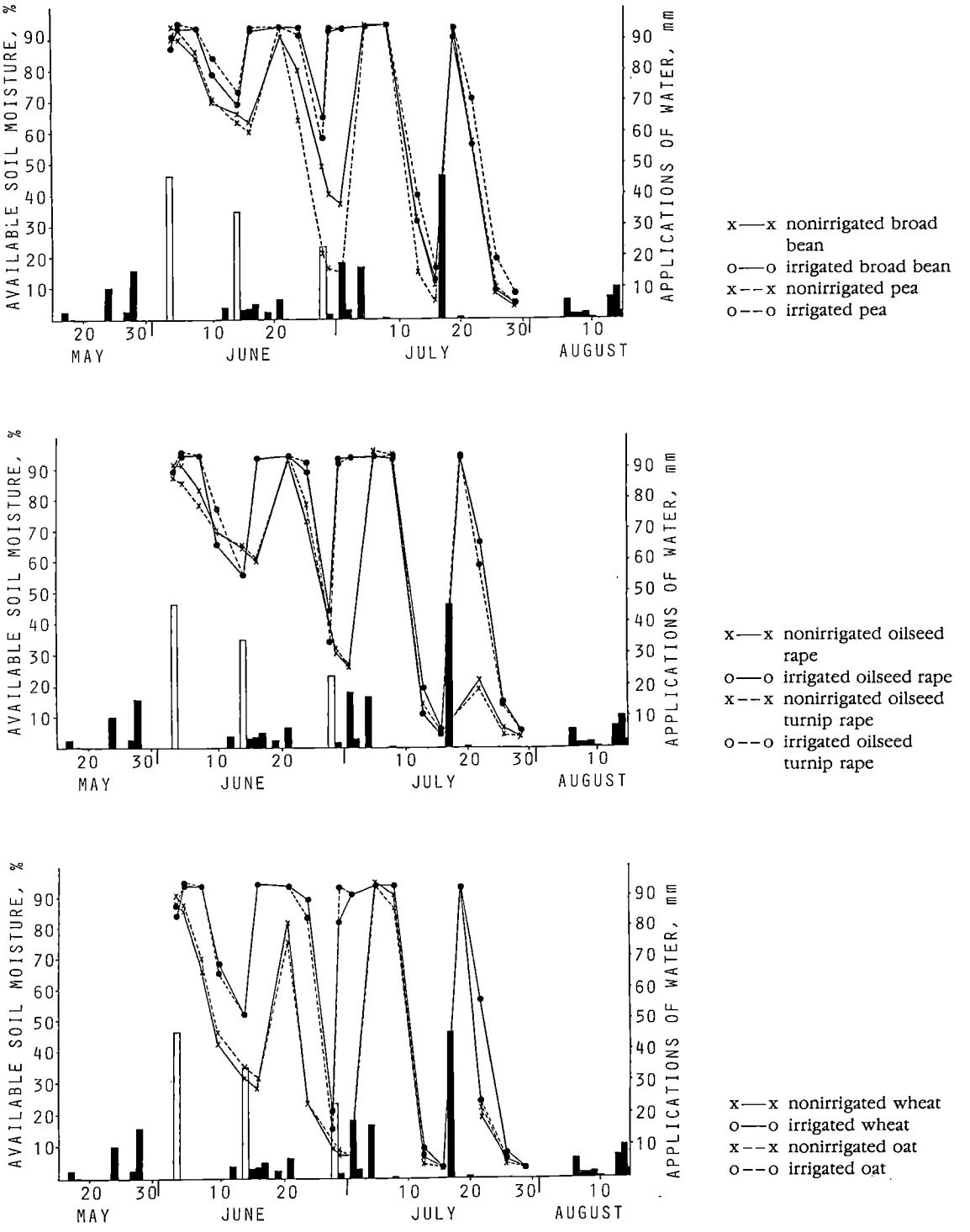
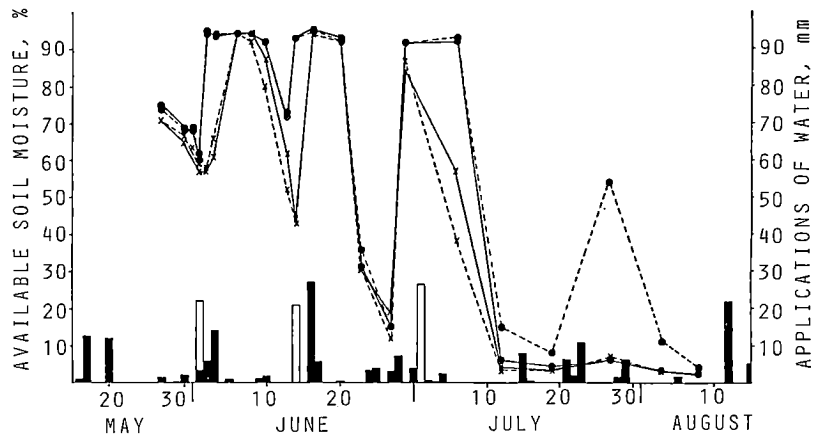
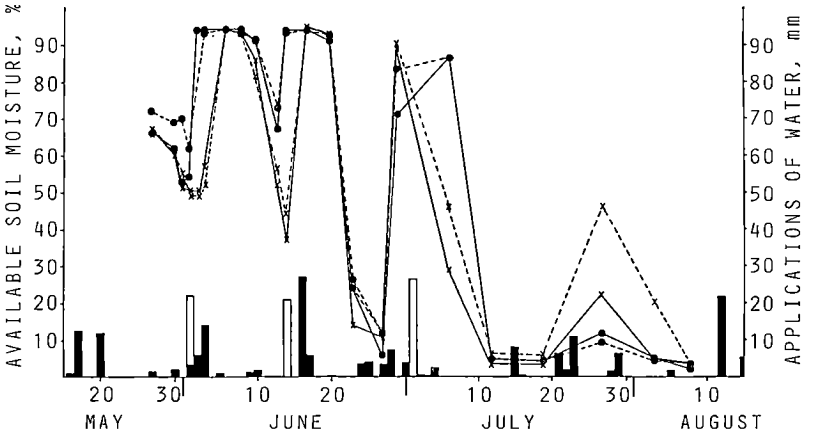



Fig. 3. Soil available water at depth of 15 cm during the 1982 growing season. Black columns show precipitation and white columns irrigations.



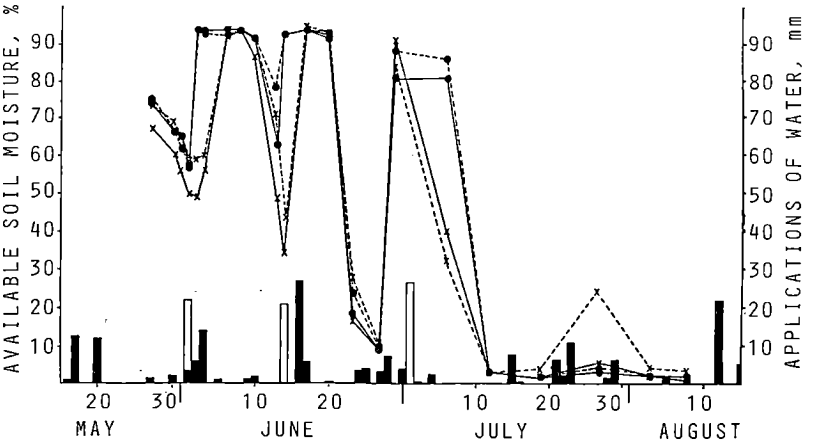




Fig. 4. Soil available water at depth of 15 cm during the 1983 growing season. Black columns show precipitation and white columns irrigations.

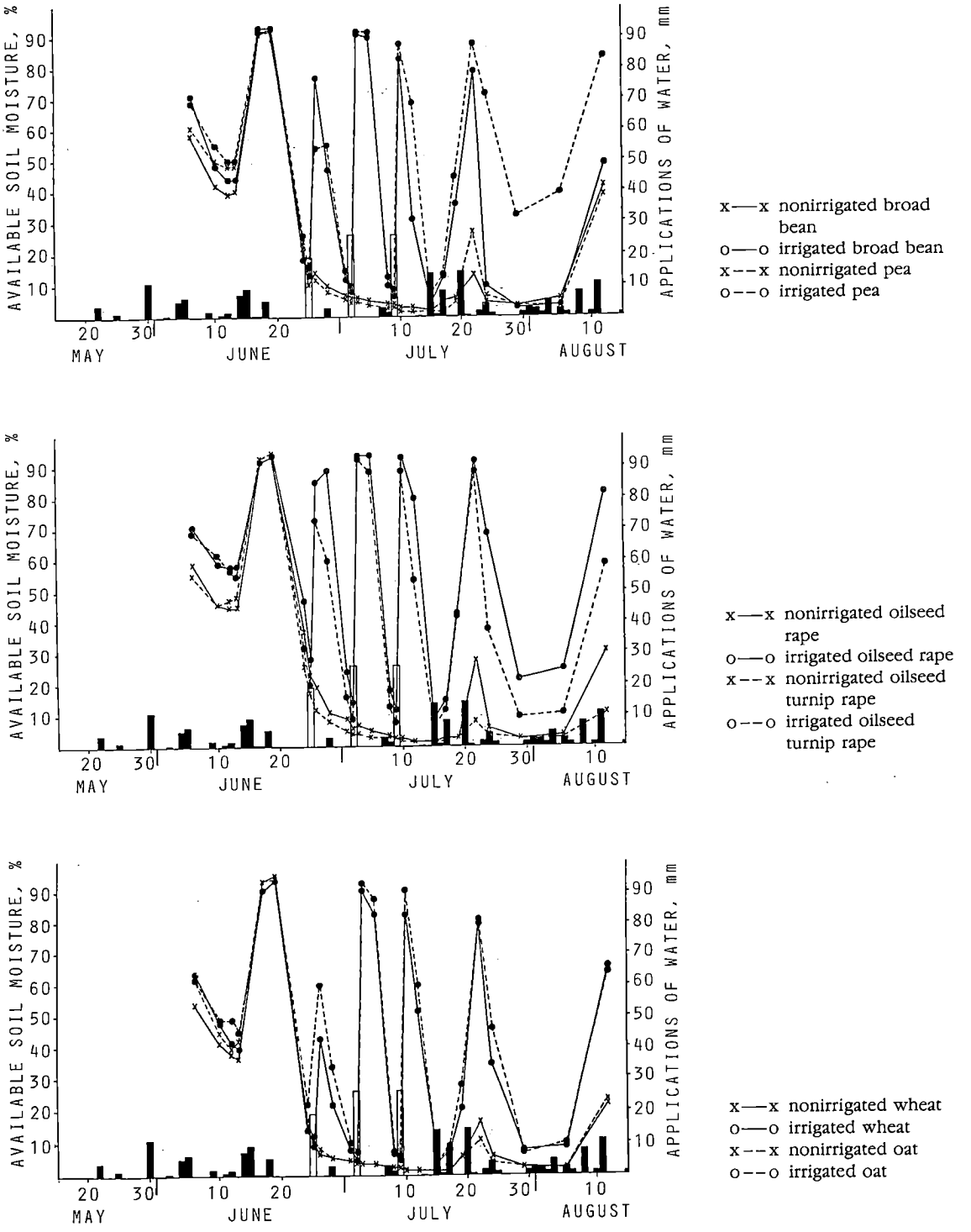



Fig. 5. Soil available water at depth of 15 cm during the 1985 growing season. Black columns show precipitation and white columns irrigations.

measured by NMR-apparatus. The weight of 1 000 seeds was calculated from the average weights of four counted lots of 100 seeds. For the cereals and the legumes, seed yields were calculated by using seed moisture of 15 %. For the rapes, seed moisture of 9 % was used.

### Statistical significance

The results were studied statistically by employing the analysis of variance and Tukey's tests HSD (Honestly Significant Difference) to find the significant ($P = 0.05$) differences between group means.

## RESULTS

### Soil moisture

The results for the soil available water during the growing seasons are shown in Figures 2—5. In 1981 and 1984, irrigation was carried out only once due to heavy rainfall. The soil was very moist during these summers, and therefore the results for these years are not shown in the figures.

Without irrigation, the available moisture decreased to 50 percent in the middle of June 1980 (Fig. 2). In July, the soil was dry even with irrigation. During this year, wheat utilized more water than pea or the rapes. This is shown especially by the July measurements.

Cereals utilized more water than legumes and the rapes also in the very rainy growing season of 1981 when the soil moisture was under the limit of 50 percent only at the beginning and in the end of June.

During the growing period of 1982, the soil moisture was below the limit of 50 percent at three different times: the end of June, the middle of July and the end of July (Fig. 3). The nonirrigated cereal plots fell below this limit also in the middle of June. The effect of the irrigations on the soil moisture was shown in June, but no clear effect persisted during July in the soil of legumes or rapes, like that in 1980—81. In the early summer, cereals utilized considerable more water than the other experimental plants.

In 1983, the irrigations of June were followed by heavy rainfall, and the effect of the irrigations on the soil moisture condition was very slight. In July, the soil moisture was much lower, and the effect of irrigation on 1st July was clear in all plots (Fig. 4). No clear differences were found, however, in water utilization among the different plants. Neither were clear differences found for the very rainy summer of 1984. Nevertheless, the effect of the only irrigation carried out was shown during two weeks at the end of June. To some extent, legumes utilized less water than did rape or oat in the middle of June.

In 1985, the soil available moisture did not decrease below 50 percent until the last week of June, but thereafter, the soil was left dry in nonirrigated plots (Fig. 5). The positive effects of three irrigations on soil moisture lasted only one week each. In the end of June, cereals utilized a little more water than did legumes or rapes.

### Seed yields

In comparison with the treatment of no irrigation, the treatment of three irrigations (104 mm) increased the broad bean yield by 750 kg/ha in 1982. This clear difference was not statistically significant (HSD = 1 000 kg/ha). In 1985, this positive effect was significant, likewise the influence by one irrigation both on 25.6 and 2.7. The third season when broad bean was irri-

Table 2. Effect of repeated applications of water on yield and quality of legumes and spring oil seeds.

| Sowing | Irrigation | | Broad bean | | | Pea | | | Turnip rape | | | | Rape | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| date | date, | mm | Yield kg/ha | 1 000 sw g | protein % | Yield kg/ha | 1 000 sw g | protein % | Yield kg/ha | 1 000 sw g | oil c. % | protein % | Yield kg/ha | 1 000 sw g | oil c. % | protein % |
| 1980 | — | — | | | | 1 170 | 211 | 22.1 | 3 140 | 2.31 | 40.6 | | 2 360 | 3.52 | 44.1 | |
| 16.5. | 2.6. | 25 | | | | 1 970 | 214 | 21.8 | 2 990 | 2.32 | 41.9 | | 2 520 | 3.31 | 45.4 | |
| | 9.6. | 39 | | | | 1 060 | 216 | 21.1 | 2 880 | 2.31 | 42.5 | | 2 380 | 3.45 | 47.0 | |
| | 16.6. | 31 | | | | 2 370 | 217 | 21.3 | 3 150 | 2.28 | 41.4 | | 2 400 | 3.30 | 44.8 | |
| | sum | 95 | | | | 990 | 212 | 20.1 | 3 040 | 2.26 | 42.9 | | 2 350 | 3.37 | 46.9 | |
| | | HSD 0.05 | | | | 1 240 | 9 | 1.9 | 350 | 0.22 | 2.7 | | 510 | 0.29 | 2.5 | |
| 1981 | — | | 5 840 | 240 | 32.3 | 1 260 | 195 | 21.0 | 2 630 | 2.39 | 41.4 | | 3 240 | 3.44 | 48.3 | |
| 15.5. | 31.5. | 29 | 6 080 | 240 | 32.2 | 1 400 | 180 | 19.7 | 2 290 | 2.31 | 43.6 | | 2 940 | 3.46 | 49.3 | |
| | | HSD 0.05 | 490 | 15 | 2.2 | 660 | 23 | 2.9 | 500 | 0.16 | 1.6 | | 460 | 0.16 | 1.1 | |
| 1982 | — | — | 3 960 | 246 | 34.1 | 3 020 | 205 | 20.1 | 2 870 | 2.34 | 41.2 | 24.2 | 3 180 | 3.58 | 45.7 | 25.0 |
| 17.5. | 3.6. | 46 | 4 560 | 254 | 34.8 | 2 470 | 203 | 18.5 | 2 760 | 2.34 | 42.5 | 21.7 | 3 130 | 3.59 | 46.8 | 23.6 |
| | 14.6. | 35 | 4 500 | 256 | 35.0 | 2 820 | 210 | 20.3 | 2 930 | 2.22 | 41.6 | 23.1 | 3 230 | 3.48 | 46.3 | 25.1 |
| | 28.6. | 23 | 4 230 | 250 | 34.2 | 2 720 | 206 | 19.7 | 2 800 | 2.33 | 41.6 | 22.9 | 3 010 | 3.53 | 46.9 | 24.1 |
| | sum | 104 | 4 710 | 257 | 35.0 | 1 240 | 203 | 18.2 | 2 340 | 2.28 | 43.1 | 20.6 | 2 430 | 3.69 | 46.3 | 24.9 |
| | | HSD 0.05 | 1 000 | 18 | 1.5 | 1 100 | 11 | 1.5 | 520 | 0.18 | 1.9 | 3.9 | 840 | 0.32 | 1.8 | 2.0 |
| 1983 | — | — | 3 430 | 208 | 30.3 | 3 280 | 251 | 23.9 | 3 060 | 2.43 | 41.7 | 25.0 | 2 180 | 4.14 | 38.3 | 25.1 |
| 12.5. | 1.6. | 22 | 3 100 | 204 | 30.3 | 2 950 | 250 | 22.7 | 2 900 | 2.41 | 43.6 | 23.1 | 1 870 | 4.19 | 48.9 | 24.3 |
| | 14.6. | 21 | 3 300 | 209 | 30.2 | 2 580 | 248 | 23.1 | 2 920 | 2.39 | 42.9 | 24.0 | 1 810 | 4.39 | 49.0 | 23.8 |
| | 1.7. | 27 | 3 760 | 210 | 31.1 | 3 050 | 250 | 23.0 | 3 080 | 2.41 | 42.6 | 24.3 | 2 180 | 4.15 | 48.2 | 24.4 |
| | sum | 70 | 3 070 | 201 | 30.4 | 2 230 | 232 | 21.0 | 2 870 | 2.42 | 43.7 | 22.7 | 1 790 | 4.26 | 49.8 | 23.0 |
| | | HSD 0.05 | 460 | 7 | 1.6 | 940 | 15 | 1.6 | 410 | 0.14 | 2.6 | 3.4 | 350 | 0.51 | 3.1 | 4.6 |
| 1984 | — | — | 2 220 | 168 | 31.3 | 1 850 | 167 | 20.5 | 3 100 | 2.65 | 44.5 | 22.7 | 2 740 | 3.00 | 44.5 | 23.2 |
| 18.5. | 12.6. | 23 | 2 370 | 173 | 31.0 | 1 800 | 162 | 18.4 | 3 010 | 2.58 | 45.2 | 22.6 | 2 740 | 3.04 | 45.9 | 22.9 |
| | | HSD 0.05 | 790 | 18 | 0.9 | 910 | 16 | 2.6 | 450 | 0.10 | 1.8 | 0.7 | 600 | 0.18 | 2.0 | 0.8 |
| 1985 | — | — | 4 140 | 214 | 32.3 | 2 340 | 212 | 21.7 | 2 910 | 2.43 | 41.9 | 24.4 | 1 920 | 3.20 | 44.9 | 23.7 |
| 24.5. | 25.6. | 19 | 4 960 | 214 | 33.3 | 2 630 | 211 | 22.1 | 2 760 | 2.35 | 43.8 | 22.7 | 1 500 | 3.32 | 45.6 | 23.4 |
| | 2.7. | 26 | 4 830 | 213 | 33.5 | 2 440 | 197 | 21.5 | 2 630 | 2.35 | 42.2 | 23.9 | 1 470 | 3.27 | 44.9 | 24.1 |
| | 9.7. | 26 | 4 620 | 214 | 33.5 | 2 400 | 187 | 21.6 | 2 720 | 2.38 | 42.1 | 23.9 | 1 690 | 3.16 | 44.5 | 23.7 |
| | sum | 71 | 5 140 | 214 | 33.4 | 2 230 | 186 | 20.6 | 2 520 | 2.33 | 41.9 | 23.7 | 1 380 | 3.15 | 46.0 | 22.8 |
| | | HSD 0.05 | 600 | 12 | 0.9 | 470 | 14 | 1.2 | 420 | 0.21 | 2.0 | 1.3 | 770 | 0.34 | 1.6 | 1.9 |

gated three times was in 1983, when one application of water (27 mm) on 1.7. caused the best yield. It was significantly better than the yields brought about by three applications or one application on 1.6. or 14.6., which were followed by natural precipitations of 20 and 30 mm, respectively. Compared with no irrigation, broad bean benefited from one application of water in the very rainy growing periods of 1981 (29 mm) or 1984 (23 mm), but only very slightly (Table 2, Fig. 6).

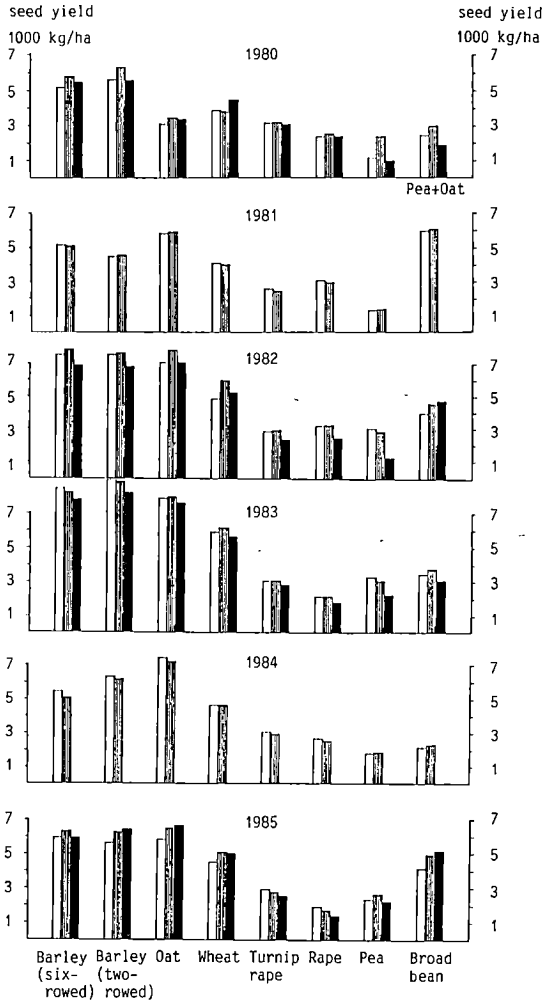



Fig. 6. Effect of irrigation on seed yields (85 % dry matter) on clay soil in Jokioinen 1980—1985.
□ = yield without irrigation
▨ = yield with one irrigation (about 30 mm) at the best time
■ = yield with three irrigations (3×30 mm)

In every experimental year, the treatment of three applications of water was harmful to pea production, even to the mixture of pea and oat in 1980. Compared with the nonirrigated plots in 1982 or 1983, three irrigations decreased the yields significantly (P = 0.05). In 1980 and 1985, the best yields were found from the treatment with one irrigation (16.6. 31 mm and 25.6. 19 mm, respectively). The negative effects of three irrigations compared with the best yields were from 1 400 to 2 000 kg/ha (Table 2, Fig. 6).

Like pea, spring oilseed rapes were sensitive to wet clay soil conditions (Table 2, Fig. 6). Compared with no irrigation, the yield was decreased by three irrigations (in 1980 there was no difference), and one application was either deleterious or neutral. Even though in 1985 the excess rainfall occurred only in August, all applications of water were deleterious to oilseed production. Nevertheless, the vegetative growth was the best on the irrigated plots. The extra water caused a large variation, and the differences between treatments were rarely significant (P = 0.05).

In wheat production, one application of water increased grain yield more than three applications, as compared with no irrigation (Table 3, Fig. 6). Only in 1980, the treatment with three irrigations (95 mm) caused the best yield which was significantly better (yield increase 1 080 kg/ha) than the yield by one irrigation on 2.6. (25 mm). The yields of the other treatments with one irrigation or that of the control were equal. In 1983, the best yield was found in the treatment with one irrigation on 1.7. (27 mm). This yield was significantly better (yield increase 520 kg/ha) than the yield caused by three irrigations (104 mm). In the almost normal year of 1985, all irrigation treatments brought about better yields (P = 0.05) compared with no irrigation.

Table 3. Effect of repeated applications of water on yield and quality of cereals.

| Sowing | Irrigation | | Wheat | | | Oat | | | Barley (two-rowed) | | | Barley (six-rowed) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| date | date, | mm | Yield kg/ha | 1000 sw protein g | % | Yield kg/ha | 1000 sw protein g | % | Yield kg/ha | 1000 sw protein g | % | Yield kg/ha | 1000 sw protein g | % |
| 1980 | — | — | 3 880 | 33.5 | 14.6 | 3 100 | 27.7 | 16.8 | 5 640 | 38.5 | 12.6 | 5 180 | 30.5 | 11.7 |
| 16.5. | 2.6. | 25 | 3 370 | 30.8 | 14.3 | 2 640 | 25.8 | 15.9 | 6 320 | 38.4 | 13.1 | 4 740 | 27.7 | 12.2 |
| | 9.6. | 39 | 3 800 | 33.7 | 13.3 | 3 060 | 27.0 | 15.6 | 5 390 | 38.3 | 12.3 | 4 870 | 30.2 | 12.1 |
| | 16.6. | 31 | 3 800 | 30.9 | 13.6 | 3 470 | 26.8 | 16.3 | 6 010 | 38.9 | 11.8 | 5 790 | 30.3 | 11.7 |
| | sum | 95 | 4 450 | 33.0 | 12.9 | 3 370 | 26.6 | 15.1 | 5 600 | 38.7 | 11.6 | 5 480 | 30.9 | 10.8 |
| | | HSD 0.05 | 890 | 3.0 | 1.2 | 1 250 | 2.6 | 1.4 | 1 160 | 4.3 | 1.4 | 1 400 | 3.6 | 1.4 |
| 1981 | — | — | 4 060 | 26.7 | 14.6 | 5 820 | 30.0 | 12.5 | 4 410 | 33.5 | 13.1 | 5 110 | 28.4 | 13.0 |
| 15.5. | 31.5. | 29 | 4 010 | 27.1 | 14.2 | 5 850 | 29.6 | 11.4 | 4 410 | 32.8 | 12.9 | 5 120 | 28.5 | 13.0 |
| | | HSD 0.05 | 530 | 2.0 | 0.8 | 480 | 2.5 | 1.2 | 390 | 3.1 | 1.3 | 350 | 1.7 | 1.2 |
| 1982 | — | — | 4 860 | 33.2 | 14.1 | 7 040 | 35.4 | 14.6 | 7 570 | 46.8 | 13.4 | 7 510 | 39.3 | 13.4 |
| 17.5. | 3.6. | 46 | 5 620 | 34.2 | 13.0 | 7 660 | 35.5 | 13.1 | 7 030 | 46.2 | 12.5 | 7 030 | 39.6 | 12.8 |
| | 14.6. | 35 | 5 960 | 34.7 | 13.1 | 7 850 | 36.1 | 13.7 | 7 490 | 47.0 | 13.7 | 7 860 | 41.3 | 13.6 |
| | 28.6. | 23 | 5 640 | 33.3 | 13.0 | 7 510 | 35.4 | 13.6 | 7 660 | 47.0 | 13.1 | 7 850 | 39.8 | 13.2 |
| | sum | 104 | 5 220 | 33.7 | 12.6 | 7 050 | 34.9 | 12.0 | 6 790 | 46.3 | 13.3 | 6 860 | 40.6 | 13.3 |
| | | HSD 0.05 | 1 290 | 2.0 | 1.5 | 1 230 | 2.5 | 1.7 | 1 100 | 1.9 | 1.2 | 1 090 | 1.6 | 1.5 |
| 1983 | — | — | 5 910 | 36.7 | 13.3 | 7 850 | 34.9 | 14.0 | 8 950 | 48.8 | 11.2 | 8 420 | 38.3 | 11.2 |
| 12.5. | 1.6. | 22 | 5 530 | 35.7 | 12.2 | 7 390 | 34.3 | 12.0 | 8 510 | 48.9 | 10.6 | 8 110 | 38.0 | 10.7 |
| | 14.6. | 21 | 5 650 | 36.3 | 12.4 | 7 400 | 35.0 | 12.6 | 8 660 | 48.9 | 11.0 | 8 170 | 37.5 | 10.7 |
| | 1.7. | 27 | 6 130 | 35.6 | 12.6 | 7 930 | 34.4 | 12.8 | 8 800 | 48.1 | 10.8 | 8 120 | 37.1 | 10.8 |
| | sum | 70 | 5 610 | 35.1 | 12.1 | 7 560 | 34.1 | 12.2 | 8 150 | 48.7 | 10.6 | 7 740 | 37.6 | 10.6 |
| | | HSD 0.05 | 470 | 1.0 | 1.2 | 610 | 1.3 | 1.2 | 670 | 1.4 | 0.9 | 640 | 2.2 | 1.1 |
| 1984 | — | — | 4 760 | 28.0 | 14.2 | 7 390 | 32.1 | 12.6 | 6 350 | 34.4 | 12.0 | 5 480 | 30.4 | 13.8 |
| 18.5. | 12.6. | 23 | 4 800 | 27.6 | 13.9 | 7 220 | 32.7 | 12.1 | 6 150 | 34.3 | 11.6 | 5 050 | 29.7 | 13.7 |
| | | HSD 0.05 | 640 | 1.5 | 0.7 | 420 | 1.3 | 1.1 | 550 | 2.5 | 0.7 | 390 | 1.3 | 1.2 |
| 1985 | — | — | 4 500 | 34.9 | 14.6 | 5 810 | 30.9 | 14.1 | 5 620 | 45.1 | 12.9 | 5 960 | 39.7 | 14.2 |
| 24.5. | 25.6. | 19 | 5 070 | 31.9 | 13.9 | 6 490 | 31.4 | 12.8 | 6 220 | 45.8 | 12.4 | 6 300 | 39.3 | 13.3 |
| | 2.7. | 26 | 4 920 | 32.0 | 14.0 | 6 290 | 32.4 | 13.4 | 6 230 | 44.5 | 12.1 | 6 310 | 40.3 | 13.5 |
| | 9.7. | 26 | 4 820 | 31.9 | 14.2 | 6 170 | 30.4 | 12.9 | 5 910 | 41.9 | 12.1 | 5 960 | 38.8 | 13.7 |
| | sum | 71 | 5 000 | 27.7 | 14.0 | 6 610 | 31.0 | 12.7 | 6 380 | 40.1 | 11.9 | 5 930 | 37.9 | 13.5 |
| | | HSD 0.05 | 300 | 3.2 | 0.8 | 510 | 2.2 | 0.8 | 550 | 2.6 | 0.6 | 520 | 2.2 | 1.0 |

Oat profited from the water applications as well as wheat, except in 1980, when oat benefited the most from one irrigation on 16.6. (31 mm), whereas wheat profited the most from the treatment with three irrigations. In 1985, the best oat yield was brought about by three irrigations. This best yield and the second best yield in the treatment of the first irrigation on 25.6. (19 mm) were significantly higher than on the nonirrigated plots. In 1983, when irrigations were followed by heavy rainfall in June, both wheat and oat benefited more ($P = 0.05$) from irrigation on 1.7. (27 mm) than on 1.6. (22 mm), and three irrigations caused the lowest yields (Table 3, Fig. 6).

There were no clear differences between the two- and six-rowed barleys. However, in 1985, tow-rowed Kustaa cultivar profited significantly from three applications of water (71 mm), whereas six-rowed Arra benefited only slightly from one application, compared with no irrigation. In 1983, three irrigations had a significant negative effect on barley production. The best yields were caused by no irrigation. In two-rowed barley, one irrigation on 1.7. (27 mm) also caused a significantly better yield than three irrigations. The same trend can be observed also in 1982, but due to the very large variation, this negative effect by three applications of water was not significant (Table 3, Fig. 6).

## Quality

The higher the broad bean seed yield increased, the better was the protein content. This effect was significant in 1985, when protein content increased from 32.3 per cent to 33.4, as the yield increase was 1 000 kg/ha by three irrigations, as compared with no irrigation. The seed weight was more constant. In 1983 the 1 000 seed weight increased from 246 g to 257 g by three irrigations, but due to the large variation this effect was not significant (Table 2).

In pea production, both the seed weights and protein contents were decreased by the irrigation treatment, likewise the seed yields. In 1985, when broad bean benefited from three irrigations, pea quality was the poorest in this treatment. In comparison with the best treatment of that year, i.e. water application (19 mm) on 25.6., the protein content of pea decreased significantly from 22.1 per cent to 20.6, while the yield decrease was 400 kg/ha by three irrigations. The 1 000 seed weight decreased from 211 g to 186 g, as well. In 1982 and 1983, when the best yields were caused by withholding irrigation, protein contents were decreased by 1.9 and 2.9 percent by three irrigations ($P = 0.05$). In 1980, also the protein content of the mixture of pea and oat was decreased by the irrigation treatments (Table 2).

The oil content of turnip rape seeds increased and the protein content decreased by the treatment of three irrigations. This effect was significant in 1982, when the oil content of the Ante cultivar was increased from 41.2 (on nonirrigated plots) to 43.1 percent by three irrigations. At the same time, the yield decrease was 530 kg/ha and the protein content fell from 24.2 percent to 20.6. Rape had a higher and more constant oil content than turnip rape. The excess water had no clear effect on the seed weights (Table 2).

In the production of wheat, three irrigations significantly decreased the protein content, regardless of the grain yields. Compared with no irrigation, the negative effect ($P = 0.05$) of water applications on the protein content (percentage units) of the Ruso cultivar was in 1980: 1.7, in 1982: 1.5 and in 1983: 1.2. In oat, where the protein content averaged about 13.5 percent, like wheat, these differences were 1.7, 2.6, 1.8, respectively, and in 1985 1.4 ($P = 0.05$). This negative effect was not clear in the grain weights. Only in 1983 and in 1985 did the weight of wheat grains decrease significantly by three irrigations (Table 3).

As in the other cereals studied, the protein content of barley was decreased by three irri-

gations. In 1985, the protein content of two-rowed Kustaa was significantly lower (11.9 percent) in this treatment, than on the nonirrigated plots (12.9 percent). In 1980, a significant negative effect was found between three irrigations and one water application on 2.6. (25 mm), both in two- (Ingrid) and six-rowed (Pomo) barleys. In 1982, the lowest protein contents were caused by an application of 46 mm water during a very cool June (3.6.). In 1985, grain weights were decreased significantly by three irrigations. On the contrary, in 1982 one irrigation on 14.6. (35 mm) caused significantly heavier grains in six-rowed barley compared with no irrigation (Table 3).

## DISCUSSION

In the years 1980—84 the precipitation deficit in May—July was unusually low. Excessive dryness of the soil occurred only in the summer of 1985, when there was no rainfall for a period of one month. Thus soil available water measurements usually showed over 50 percent of the soil available water capacity, which is considered the limit of water deficit (ELONEN et al. 1967 a). Soil moisture was usually lower than this limit only in the end of June or at the beginning of July, when the irrigation treatments were carried out.

According to the measurements of soil available water, cereals utilized more water in the early summer than did legumes or oilseed rapes. It follows that cereals could profit the most from irrigations before the end of June. In addition, broad bean made surprisingly good use of the excess water, even in June. The present investigation shows, that broad bean needs a plentiful supply of water in order to produce a high seed yield of good quality.

On the contrary, another experimental leguminous plant, pea, was very sensitive to three irrigations, but also to one application of water, if the treatment was followed by rainfall or low temperatures. Protein content decreased with seed yield due to excessively heavy applications of water.

RICHARDS and THURLING (1978) reported that the seed yield of oilseed rapes is lowest when drought is occurred either from stem elongation or from the period of anthesis. In the present study such a dry period occurred in June—July 1985, but seed production was not sensitive to this drought. On the contrary, the applications of water only induced the growth of vegetative parts, and decreased the seed yield. According to LINNER (1981), irrigation may favour only vegetative growth, even if it can increase the production of spring oilseed rapes during dry Nordic summers (ELONEN 1974). According to this study, spring oilseed rapes are more sensitive to wet soil conditions than to moderate drought.

It is very probable that in the present study irrigation reduced the amount of fertilizer nitrogen due to denitrification or leaching, as in the other experiments reported by KAILA and ELONEN (1971) or TURTOLA and JAAKKOLA (1985). Therefore it is understandable that the protein content of rape seeds was decreased by the irrigations, whereas oil content was increased, which is in agreement with LINNER (1981) or KROGMAN and HOBBS (1975). This effect was clear not only in the treatments with three irrigations, but also with one water application at the beginning of June. Seed weight was not clearly increased along with oil content, even though a positive correlation should exist between them (RUSSELL and KUZINA 1976).

According to previous studies (ELONEN et al.

1967 c, ELONEN and KARA 1972, LINNER 1974, HAUGE et al. 1981), irrigation decreases the protein content of cereals while grain yields increase. This was also shown by the present study in the years 1980 and 1985, but due to possible losses of nitrogen, the negative effect due to excess water on both protein content and cereal yield was also very clear.

During dry summers irrigation has increased the 1 000 grain weights (POHJANHEIMO and HEINONEN 1960, ELONEN and KARA 1972). In the present study, irrigation had the opposite effect on grain weights due to natural precipitation. This finding agrees with those of HAUGE et al. (1981). Even in 1985, when July was dry, irrigations decreased the grain weights of wheat and barleys. Irrigation had a positive effect on grain weight only in the six-rowed barley in the dry and cool June of 1982.

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*Manuscript received October 1990*



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SELOSTUS

# Peltokasvien sadetus normaalia kosteampina kasvukausina

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Maatalouden tutkimuskeskus

Vuonna 1980 perustettiin laaja kuusivuotinen peltokasvien sadetuskoe hiesusavimaalle Jokioisiin. Tutkimuksessa verrattiin sadetuksen määrän (kerran 30 mm tai 3 × 30 mm) ja ajankohdan vaikutusta eri peltokasvien sadon määrään ja laatuun. Koekasveina olivat herne ja härkäpapu, kevätrypsi- ja rapsi, monitahoinen ja kaksitahoinen ohra sekä kaura ja kevätvehnä.

Maan kosteustilaa seurattiin kipsiblokkimittauksin, ja sadetukset tehtiin kaikille kasvustoille samanaikaisesti silloin, kun maan kasveille käyttökelpoisen veden määrä oli lähellä 50 % hyötykapasiteetista. Alkukesällä maa kuivui ensimmäiseksi viljakasvustoissa.

Koska koevuosien 1980—1985 kasvukaudet olivat poikkeuksellisen kosteita, liika märkyys tuli kasvua rajoittavaksi tekijäksi. Siten tutkimus selvitti eri peltokasviemme kasvukykyä ja laadun kehittymistä märissä olosuhteissa.

Härkäpapu hyötyi eniten sateisten kesien sadetuksista. Joka vuosi kertasadetus nosti sadon määrää ja vain vuonna 1983 kolme sadetuskertaa heikensi tulosta. Samoin härkäpavun valkuaispitoisuus ja siementen paino nousivat sadettamalla.

Herne oli taas hyvin herkkä liialle vedelle, ja joka vuosi kolme sadetuskertaa laski hernesadon määrää ja huononsi laatua. Ainoastaan vuosien 1980 ja 1985 kertasadetukset juhannuksen aikoihin olivat edullisia.

Herneen tavoin kevätöljykasvit olivat herkkiä savimaan märkyydelle. Kolme sadetuskertaa laski joka vuosi sadon määrää, ja kertasadetus oli joskus haitaksi ja joskus vailla merkitystä. Siementen öljypitoisuus nousi ja valkuaispitoisuus laski sadetettaessa.

Alkukesällä kevätviljat ottivat palko- ja öljykasveja enemmän vettä. Sadonmuodostuksessa viljat käyttivätkin kesäkuun sadetukset paremmin hyväkseen kuin herne tai öljykasvit. Viljoista vehnä oli hieman kestävämpi liikaa märkyyttä vastaan kuin kaura tai ohra. Sateisten kesien sadetukset alensivat hieman jyvien painoa.

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 375—388 (1991)

Seria AGROGEOLOGIA ET -CHIMICA N. 164 — Sarja MAA JA LANNOITUS n:o 164

# WOOD, BARK, PEAT AND COAL ASHES AS LIMING AGENTS AND SOURCES OF CALCIUM, MAGNESIUM, POTASSIUM AND PHOSPHORUS

INTO SAARELA

SAARELA, I. 1991. **Wood, bark, peat and coal ashes as liming agents and sources of calcium, magnesium, potassium and phosphorus.** Ann. Agric. Fenn. 30: 375—388. (Agric. Res. Centre of Finland, Inst. Crop and Soil Sci., SF-31600 Jokioinen, Finland.)

The capacities of different ashes as both liming agents and nutrient sources for rye grass, barley and oats were studied in pot and field experiments during 1980—1986. Wood ash proved to be an efficient and fastly acting liming agent and also rich in nutrients. High application rates of wood ash supplied K in excess consequently decreasing the Ca contents of plants. Industrial bark ashes were usually diluted with organic residues and moisture, and were much poorer in K. The ashes of the fossil fuels, peat and coal, exerted minor liming effects and were poor in nutrients. Due to its high relative content of soluble Mg, coal ash increased plant Mg contents excessively and decreased plant Ca contents when applied in large rates. The results obtained suggest that the liming efficiency of ashes can be most accurately estimated by means of an acid-base titration method and that the nutrients available to plants may be most reliably assessed employing a selective extractant such as citric acid.

Index words: wood ash, bark ash, peat ash, coal ash, liming agent, soil pH, calcium, magnesium, potassium, phosphorus, barley, oat, rye grass, nutrient uptake.

## INTRODUCTION

Ashes contain plant nutrients in the form of basic compounds. Thus, they act as both liming agens that correct soil acidity and as fertilizers which supply mineral nutrients to plants. Plant ashes, which are composed of the mineral elements taken up from the soil by plant roots, are known to be valuable soil amendments (HAKKILA and KALAJA 1983, HUOKUNA et al. 1988, SAARELA 1989). Wood ashes have been highly valued potassium fertilizers in the past (SHUTT 1935). Fossil fuels originate from ancient plants, but have lost a major part of their nutrients during geologic alterations. Peat and coal ashes are mostly composed of insoluble aluminium and iron silicates, but usually exert minor liming effects and supply some nutrients (MARTENS et al. 1970, JOKINEN 1982, AITKEN et al. 1984, HARTIKAINEN 1984, KATZUR and GORA 1986).

Wood and bark ashes are agronomically the most important ash types currently in Finland (HAKKILA and KALAJA 1983). These waste materials have not been studied as comprehensively in the international research as coal ashes, and would therefore need additional investigation in order to become successfully utilized substitutes for lime and fertilizers (OHNO and ERICH 1990). Fossil ashes, which may sometimes be mixed with plant ashes, have also been studied little in Finnish conditions. Therefore the effects of ten different ash samples on soils

and plants were investigated in four pot experiments and in two field experiments. The yield results of these experiments have been published earlier (SAARELA 1989). The liming effects and macronutrient supply by the ashes are presented in this paper.

## MATERIAL AND METHODS

**Ashes.** The ash material selected for the study included two samples of wood ash, four wood bark ashes, two peat ashes, and one lot of coal ash (Table 1). One straw ash was preliminarily tested in the first experiment. The different ashes had very variable compositions of total and soluble macronutrients. The nutrients soluble in 2 % citric acid were extracted from 1—3 g of ash in 100 ml of the extraction for one hour, and the HCl-soluble nutrients were measured from the HCl extracts of the acid neutralization capacity procedure explained earlier (SAARELA 1989). Phosphorus was determined from the extracts colorimetrically by the vanadate method, and the cationic elements were measured by AAS (KÄHÄRI and NISSINEN 1978). The total contents were obtained by the HCl-$HClO_4$-HF digestion method as reported in the earlier paper (SAARELA 1989) which also gives more detailed information about the origin and composition of the ashes.

**Experiments.** The pot experiments were established using nutrient deficient acid soils in order to test ashes as all-round soil amendments. In the first pot experiment (P1), four ashes were studied as nutrient sources for rye grass in an acid Carex peat. In the second pot experiment, in the same soil (P2), six ashes were compared in barley and oats. Pot experiment P3 was particularly aimed at testing the availability of phosphorus in three different ashes. The fourth pot experiment (P4) was conducted chiefly for testing a pelletted sample of bark ash. Increasing rates of wood ash were compared with ground limestone and P and K fertilizers in two field experiments in clay (F1) and mull (F2) soils. A more detailed experimental description has been presented in the previous paper (SAARELA 1989). The dried yield samples were ground and analyzed for Ca, Mg, K and P (KÄHÄRI and NISSINEN 1978). Soils were tested for pH, electrical conductivity and extractable Ca, Mg, K and P using the acid ammonium acetate method (VUORINEN and MÄKITIE 1955). The reliability of the results obtained from four replicates were tested by means of the analysis of variance and the least significant differences (LSD) calculated at the risk level of 5 %.

## RESULTS

### Nutrient availability to rye grass

The extremely poor initial nutrient status of the acid Carex peat used in pot experiment P1 resulted in a very wide variation in the amounts of nutrients taken up by rye grass (Appendix 1). The large differences obtained between the treatments strikingly displayed the diversity of the ash material. The Ca amounts in the applied rates of wood, bark and peat ashes were comparable to those added in ground limestone, however, rye grass had a much lower uptake of this nutrient from the ash-treated soils than from the limed soils (Appendix 1). In the cases

Table 1. pH of 1 % water suspension, acid neutralization capacities as determined by titration and as calculated from HCl-soluble Ca + Mg contents as well as total and soluble contents of nutrients in ashes. (HCl = soluble in 0.5 M HCl at 100 °C, Hcitr. = soluble in 2 % citric acid).

| Origin and number | pH | Neutr. capac. % Ca | | Calcium g/kg | | | Magnesium g/kg | | | Potassium g/kg | | | Phosphorus g/kg | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | titrat. | Ca + 1.65 Mg | total | HCl | Hcitr. | total | HCl | Hcitr. | total | HCl | Hcitr. | total | Hcl | Hcitr. |
| Straw ash 1 | 10.3 | 10.8 | 4.4 | 32 | — | — | 7.0 | — | — | 240.0 | — | — | 11.7 | — | — |
| Wood ash 2 | 10.7 | 38.3 | 31.9 | 252 | 250 | 250 | 42.4 | 42.1 | 41.7 | 116.2 | 116.0 | 115.8 | 17.7 | 17.5 | 14.5 |
| Bark ash 3 | 10.3 | 22.6 | 21.4 | 189 | 187 | 179 | 16.4 | 16.2 | 13.5 | 34.6 | 21.2 | 11.3 | 8.3 | 8.0 | 7.4 |
| Peat ash 4 | 8.2 | 4.2 | 4.6 | 40 | 38 | 22 | 5.8 | 4.9 | 1.7 | 12.3 | 3.4 | 0.8 | 11.1 | 11.0 | 5.7 |
| Bark ash 5 | 10.1 | 20.1 | 18.2 | 162 | 162 | 160 | 13.2 | 12.2 | 12.2 | 17.4 | 16.8 | 16.0 | 6.0 | 6.0 | 5.1 |
| Coal ash 6 | 10.4 | 4.6 | 4.3 | 26 | 24 | 21 | 12.3 | 11.7 | 8.4 | 20.2 | 3.3 | 0.3 | 1.2 | 1.1 | 0.9 |
| Wood ash 7 | 12.0 | 31.4 | 26.2 | 213 | 212 | 213 | 32.3 | 30.5 | 30.3 | 86.1 | 85.8 | 85.2 | 17.5 | 17.3 | 11.4 |
| Bark ash 8 | 11.0 | 28.2 | 27.4 | 237 | 235 | 236 | 28.3 | 23.6 | 20.8 | 51.4 | 43.2 | 37.3 | 13.5 | 13.0 | 10.2 |
| Peat ash 9 | 8.9 | 6.6 | 10.0 | 82 | 78 | 62 | 13.6 | 13.1 | 4.3 | 11.9 | 4.3 | 3.7 | 12.4 | 11.8 | 9.1 |
| Bark ash 10 | 9.6 | 23.0 | 24.1 | 211 | 211 | 189 | 19.1 | 18.3 | 14.6 | 28.6 | 26.9 | 24.6 | 12.7 | 12.6 | 9.3 |

Table 2. Total amounts of nutrients applied in lime or ashes and fertilizers in the first year as well as soil pH values and dry matter yields of barley and oats in pot experiment P2.

| Treatment | Lime or ash g/l of soil | In lime or ash (A) or fertilizers (F) mg/l soil | | | | Soil pH months after treatment (in 0.01 M $CaCl_2$ suspension) | | | | Yield g/l soil | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcium A | Magnesium A/F | Potassium A/F | Phosphorus A/F | 1 | 4 | 16 | 28 | 1st year barley | 1 + 2 + 3 y b + o + b |
| L1F1 | 4.8 gr. limest. | 1 630 | 7/40 | 4/200 | 1/40 | 4.6 | 4.5 | 4.5 | 4.2 | 16.5 | 57.2 |
| A1WA2 | 4.2 wood ash 2 | 1 058 | 178/ 0 | 488/ 0 | 74/40 | 5.0 | 4.3 | 4.2 | 4.0 | 16.6 | 48.5 |
| A1PA4* | 14.0 peat ash 4 | 2 000 | 81/40 | 172/200 | 155/ 0 | 4.8 | 4.6 | 4.6 | 4.3 | 14.2 | 56.3 |
| A1BA5 | 8.0 bark ash 5 | 1 296 | 106/ 0 | 139/200 | 48/40 | 4.8 | 4.3 | 4.2 | 4.0 | 13.9 | 41.6 |
| A1CA6 | 34.8 coal ash 6 | 905 | 428/ 0 | 703/200 | 42/40 | 4.5 | 4.3 | 4.5 | 4.3 | 13.2 | 52.8 |
| L2F1 | 9.6 gr. limest. | 3 220 | 14/40 | 8/200 | 2/40 | 5.8 | 5.7 | 5.7 | 5.3 | 13.6 | 51.0 |
| L2F2 | 9.6 gr. limest. | 3 220 | 14/80 | 8/400 | 2/90 | 5.8 | 5.7 | 5.7 | 5.3 | 19.0 | 58.6 |
| A2WA2 | 8.4 wood ash 2 | 2 116 | 356/ 0 | 976/ 0 | 149/20 | 6.2 | 5.4 | 5.1 | 5.0 | 16.9 | 48.0 |
| A2BA3 | 14.0 bark ash 3 | 2 646 | 230/ 0 | 484/200 | 116/ 0 | 5.6 | 5.4 | 5.4 | 5.2 | 18.6 | 57.9 |
| A2BA3P | 14.0 bark ash 3 | 2 646 | 230/ 0 | 484/200 | 116/40 | 5.5 | 5.4 | 5.4 | 5.1 | 20.1 | 63.0 |
| A2BA5 | 16.0 bark ash 5 | 2 592 | 211/ 0 | 278/200 | 96/20 | 5.8 | 5.4 | 5.2 | 5.0 | 20.0 | 49.9 |
| A2CA6 | 69.6 coal ash 6 | 1 810 | 856/ 0 | 1 406/200 | 84/ 0 | 5.3 | 5.2 | 5.4 | 5.1 | 13.6 | 54.2 |
| A2CA6P | 69.6 coal ash 6 | 1 810 | 856/ 0 | 1 406/200 | 84/40 | 5.3 | 5.2 | 5.3 | 5.1 | 13.4 | 57.1 |
| LSD | | | | | | 0.14 | 0.11 | 0.12 | 0.10 | 2.0 | 5.2 |

* 14 g peat ash and 3.6 g $CaCO_3$

of bark and peat ashes, this difference can be partly explained by smaller yields, but the inefficient Ca uptake from soil after wood ash application must have been caused by some other factor. The grass produced by the low-Ca straw ash contained less Ca than did the grass grown in unlimed soil, gave additional evidence of some retarding effect by ash on Ca uptake.

Ash and soil analyses (Table 1, Appendix 1) did not suggest that a too low solubility of Ca in ashes was the primary cause of decreased Ca uptake in this acid peat soil. However, less Ca was taken up when K was applied in $K_2SO_4$ or $K_2CO_3$ compared to KCl (Appendix 1). The importance of the form and amount of applied K was even more evident in the Ca contents of plant dry matter in the first cut, as indicated by the following result of selected treatments:

| K application | | DM yield | K in DM | Ca in DM |
|---|---|---|---|---|
| form | mg/l | g/pot | g/kg | g/kg |
| KCl | 200 | 16.6 | 52 | 6.0 |
| KCl | 400 | 16.4 | 70 | 5.5 |
| $K_2SO_4$ | 400 | 17.4 | 69 | 4.3 |
| $K_2CO_3$ | 400 | 18.2 | 66 | 4.0 |
| Straw ash | 480 | 12.5 | 79 | 2.3 |
| Straw ash | 960 | 17.9 | 77 | 2.2 |
| Wood ash | 232 | 14.9 | 63 | 3.8 |
| Wood ash | 465 | 19.3 | 68 | 3.1 |

The same factors that affected Ca uptake obviously also reduced the amounts of Mg taken up from the ash-treated soils. The yields from the pots fertilized with $MgSO_4$ had higher contens of this nutrient than those produced by wood ash with much larger amounts of soluble Mg (Appendix 1). According to the soil analyses, the initially poor Mg status of the peat was substantially improved by wood, bark and peat ashes, but not by straw ash.

Because the grass efficiently extracted available K from the peat soil, the amounts taken up quite accurately indicated the supply of this macronutrient from the ashes (Appendix 1). However, straw ash was so abundant a source that it also increased the residual reserves in soil. As expected after the chemical ash analyses (Table 1), potassium seemed to have been released quantitatively from the straw and wood ashes, but only by roughly 20 % from the sand-mixed bark ash and by 4 % from the peat ash (Appendix 1).

### Soil pH and nutrients in barley and oats

The quantities of different ashes mixed into the acid Carex peat in pot experiment P2 were equivalent to ground limestone at the levels of 1.6 and 3.2 g of "neutralizing Ca" per liter of soil by the titration method. The chemically predicted efficiencies agreed with the pH values measured from the treated soils, but not very accurately (Table 2). The relative effects on pH were also strongly time dependent. Wood ash acted faster, but was eventually inferior to the chemically equivalent amounts of ground limestone. The decline in pH values during the 28-month study was best buffered by coal ash. This weak liming agent was relatively more efficient at the lower pH level. The most probable reason for these results was increased reactivity of the hydrous oxides of aluminium and iron with decreasing pH.

Ash application decreased the contents of Ca by barley substantially in the first year, but less during the later years in oats and barley (Appendix 2). Of the five ashes, the most efficient depressors of Ca absorption were wood ash with a high K content and coal ash which caused abnormally high contents of Mg in plants. These two ashes supplied less soluble Ca than the other materials did, but this was probably not the main reason for the lowered Ca content of barley, because they improved the Ca status of soil to a sufficient level.

Wood and bark ashes supplied rather substantial amounts of exchangeable Mg to the soil, but were again less effective than $MgSO_4$ in increasing plant Mg contents. Coal ash has a total Mg content of 12.3 g/kg, being high enough to excessively increase plant Mg contents after

the heavy application of coal ash in the initially very infertile peat soil (Appendix 2). The amounts of potassium supplied by the different ashes varied widely. The total amounts of K (Table 2) did not reliably predict the effects that were analytically detected in plants and soils.

The amounts of P applied via the highly varying ash material were quite equal, because P contents correlated with Ca contents and neutralizing capacities which served as the basis in ash dosing (Table 2). The rather strong growth and reasonable P uptakes of barley in the absence of other applied P proved that the bark ash 3, peat ash 4 and coal ash 5 were quite useful P sources to barley in acid peat soil (Appendix 2). However, both the plant uptakes of P and extractable P contents in soil were increased less by ashes than by the soluble fertilizer, if compared on the basis of the total amounts of P applied.

### Nutrient availability at higher pH

The annual treatments with lime and ashes in pot experiment P3 raised the soil pH values to a slightly basic level (Table 3). Wood ash 7 and bark ash 8 were comparable to the control treatments with ground limestone in acid soil. At basic pH level these ashes were superior to lime. Peat ash 9 increased the pH value of soil with a relative efficiency of only fifty per cent of its chemically determined effect. This material increased the electrical conductivity of soil more than the other agents did, and therefore evidently raised the water pH value relatively less compared to its base content. The high contents of Ca and Mg in the peat ash remained largely non-exchangeable in the soil (Appendix 3).

The Ca contents of plants were lowest with the wood ash, which supplied K in excessive amounts, while the bark and peat ashes appeared comparable to ground limestone as sources of Ca to oats and barley (Appendix 3). Large rates of K in wood ash and in KCl also decreased the contents of Mg in plants. The high rates of Mg applied in peat ash were very inefficient in increasing plant Mg contents, even though this treatment had the lowest level of K. Peat ash contained a considerable amount of K, but only a minor fraction of the total amount was available to plants. Also, the bark ash 8 had a marked fraction of unavailable K.

The yield levels of the treatments were largely determined by the availability of P in the initially P deficient soil. Ashes seemed to be the better P sources the lower the soil pH was, because P uptakes decreased from year to year through repeated treatments which increased

Table 3. Chemically determined liming effects, soil pH values and electrical conductivities as well as dry matter yields in pot experiment P3, 1st year oats, 2nd year barley, 3rd year oats.

| Annual treatment | Lime or ash g/l of soil | Neutr. capacity g Ca/l of soil | pH-$CaCl_2$ 1st year | pH-$H_2O$ 2nd year | Electr. cond.* 2nd year | Dry matter yield g/l of soil | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 1st year | 2nd year | 3rd year |
| L1 | 3.6 g gr. limest. | 1.20 | 5.3 | 6.3 | 9.1 | 18.5 | 19.5 | 27.5 |
| L2 | 7.2 g gr. limest. | 2.40 | 6.2 | 7.1 | 9.2 | 23.9 | 23.9 | 28.4 |
| WA1 | 3.6 g wood ash 7 | 1.13 | 5.2 | 6.3 | 3.4 | 22.5 | 19.7 | 17.7 |
| WA2 | 7.2 g wood ash 7 | 2.26 | 6.0 | 7.4 | 6.6 | 23.2 | 21.6 | 20.8 |
| BA2 | 7.2 g bark ash 8 | 2.03 | 6.2 | 7.5 | 3.5 | 21.3 | 19.4 | 23.4 |
| PA2 | 36.0 g peat ash 9 | 2.38 | 5.3 | 5.8 | 17.6 | 22.5 | 23.0 | 25.9 |
| LSD | | | 0.1 | 0.1 | 2.2 | 1.9 | 2.5 | 3.3 |

* $10^{-4}$ S $cm^{-1}$ in soil water suspension 1:2.5 (v/v)

Table 4. Total dry matter yield and nutrient uptake of barley and oats as well as soil analysis data after cropping in pot experiment P4. Treatments: L = ground limestone, WA = wood ash 7, BA = bark ash 10 (Table 1).

| Treatment g/l soil | | DM yield g/l of soil | Nutrient uptake, mg/l of soil | | | | Soil pH ($H_2O$) | Electr. cond. $10^{-4}$ s $cm^{-1}$ | Extractable nutrients, mg/l | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Ca | Mg | K | P | | | Ca | Mg | K | P |
| Control | | 2.2 | 11 | 22 | 226 | 84 | 4.1 | 15.9 | 276 | 269 | 829 | 159 |
| L 1/4 | 0.8 | 23.1 | 68 | 58 | 473 | 134 | 4.3 | 3.4 | 514 | 188 | 136 | 13 |
| WA 1/4 | 0.8 | 26.2 | 54 | 59 | 583 | 177 | 4.5 | 3.2 | 680 | 229 | 177 | 10 |
| BA 1/4 | 1.6 | 16.2 | 24 | 34 | 383 | 109 | 4.6 | 4.3 | 464 | 241 | 327 | 23 |
| L1 | 4.0 | 43.2 | 202 | 93 | 491 | 129 | 5.4 | 4.0 | 2 003 | 172 | 110 | 10 |
| WA1 | 4.0 | 43.6 | 170 | 99 | 775 | 181 | 5.1 | 4.5 | 1 360 | 343 | 140 | 15 |
| BA1 | 8.0 | 31.1 | 53 | 53 | 573 | 107 | 4.3 | 3.4 | 737 | 252 | 112 | 19 |
| L4 | 16 | 44.4 | 231 | 86 | 512 | 113 | 7.1 | 6.3 | 10 510 | 270 | 111 | 31 |
| WA4 | 16 | 39.3 | 91 | 81 | 1 235 | 129 | 8.2 | 10.3 | 6 114 | 1 039 | 1 038 | 297 |
| BA4 | 32 | 41.4 | 106 | 75 | 930 | 102 | 5.9 | 5.6 | 2 529 | 418 | 169 | 66 |
| WA8 | 32 | 9.4 | 11 | 20 | 450 | 23 | 9.5 | 25.9 | 13 028 | 1 844 | 4 447 | 703 |
| BA8 | 32 | 42.8 | 99 | 70 | 1 013 | 105 | 7.3 | 10.0 | 4 406 | 708 | 561 | 85 |
| BA1-P | | 7.7 | 30 | 22 | 317 | 11 | 5.0 | 15.3 | 1 385 | 382 | 802 | 25 |
| BA1L1-P | | 6.9 | 24 | 10 | 201 | 7 | 6.3 | 16.5 | 3 190 | 404 | 716 | 20 |
| BA1L1 | | 45.5 | 187 | 87 | 597 | 118 | 6.4 | 5.7 | 3 175 | 302 | 138 | 32 |
| LSD | | 2.5 | 16 | 7 | 59 | 26 | 0.3 | 0.9 | 197 | 32 | 30 | 6 |

Basic fertilization (mg/l soil): 300 K and 80 P annually, Mg 80 in 1985 and 40 in 1986

the soil pH (Appendix 3). The soil analysis employing the Finnish acid ammonium acetate method did not reliably indicate the availability of this nutrient to plants in the peat subsequent to ash application. The P test values determined after the treatments with large rates of ash were too high compared to the nutrient supply determined biologically by plants.

In the unhumified Sphagnum peat in pot experiment P4, large amounts of wood ash greatly decreased the uptakes of Ca in plants, put had a minor effect on plant Mg (Table 4). The uptake of P decreased by 30 % when the rate of wood ash was increased from 4 g/l to 16 g/l and soil pH rose from 5.1 to 8.2, though the extractable soil P rose from 15 mg/l to 297 mg/l. Pelletted bark ash (10) was a very unavailable source of Ca and P to barley and oats.

### Wood ash in clay and mull fields

The dolomitic limestone and wood ash 7 used in the field experiments (Tables 5 and 6) contained roughly speaking the same amount of Ca, 1 250 kg/6 tons, while the content of Mg was about threefold in the former (L6 = 600 kg and WA6 = 195 kg Mg/ha). The amount of K applied in the wood ash were 258 kg in 3 tons, 516 kg in 6 tons and 1 032 kg in 12 tons. The K fertilizer rates amounted to 160 kg of K/ha (treatments PK and L6PK) or 240 kg of K/ha (treatment K), and the P fertilizer rates were 120 kg/ha (treatments PK and L6PK) or 180 kg/ha (treatment P) of P during the whole experimental period. The total amounts of P in the wood ash were 53 kg in 3 tons, 105 kg in 6 tons and 210 kg in 12 tons.

On the initially more fertile field soils, the mineral composition of barley was much less affected than in the pot experiments, but changes in the mineral contents to the same directions were usually observed (Table 5). In the first year, the Ca contents were slightly decreased by large amounts of K applied via the

Table 5. Nutrient contents (g/kg) of boot stage tissue (1982 and clay 1983) and sprouts of barley in field experiments F1 (clay) and F2 (mull). L6 = dolomite lime 6 t/ha, WA3, WA6 and WA12 = 3, 6 and 12 t/ha wood ash 7. P and K fertilization annually, but not PK and L6PK treatments in 1983.

| Treatment | 1982 | | | | 1983 | | | | 1984 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ca | Mg | K | P | Ca | Mg | K | P | Ca | Mg | K | P |
| Control | 5.1 | 1.6 | 36.6 | 3.8 | 7.2 | 1.9 | 42.1 | 3.9 | 7.0 | 2.2 | 37.5 | 4.1 |
| P (60 kg/ha) | 5.5 | 1.7 | 37.2 | 4.3 | 7.9 | 2.0 | 41.7 | 4.3 | 7.2 | 2.2 | 37.6 | 4.5 |
| K (80 kg/ha) | 5.6 | 1.7 | 43.2 | 3.8 | 7.8 | 1.8 | 52.1 | 4.2 | 7.0 | 1.9 | 45.2 | 4.2 |
| PK | 5.4 | 1.7 | 41.4 | 3.9 | 7.6 | 1.9 | 44.5 | 4.3 | 7.1 | 1.9 | 43.0 | 4.4 |
| L6PK | 5.6 | 1.7 | 42.4 | 3.7 | 7.5 | 1.9 | 44.4 | 4.2 | 7.0 | 1.9 | 43.2 | 4.4 |
| WA3 | 5.0 | 1.6 | 40.0 | 3.9 | 7.3 | 1.9 | 43.0 | 4.2 | 7.1 | 2.1 | 37.9 | 4.1 |
| WA6 | 4.9 | 1.6 | 42.2 | 3.8 | 7.5 | 1.9 | 46.1 | 4.5 | 7.0 | 2.0 | 39.3 | 4.3 |
| WA12 | 5.0 | 1.6 | 42.7 | 3.7 | 7.6 | 1.9 | 47.3 | 4.7 | 7.1 | 2.0 | 42.7 | 4.6 |
| LSD | 0.6 | 0.2 | 5.0 | 0.4 | 0.6 | 0.2 | 3.0 | 0.4 | 0.4 | 0.2 | 3.1 | 0.3 |
| | | | | | Clayey mull (F2) | | | | | | | |
| Control | 6.4 | 1.5 | 43.4 | 2.6 | 3.7 | 1.2 | 28.6 | 2.3 | (not analyzed) | | | |
| P | 6.0 | 1.5 | 42.7 | 2.6 | 4.0 | 1.1 | 30.4 | 2.2 | | | | |
| K | 6.0 | 1.5 | 43.6 | 2.7 | 3.5 | 1.0 | 29.0 | 2.2 | | | | |
| PK | 5.8 | 1.4 | 41.6 | 2.4 | 3.8 | 1.1 | 26.6 | 2.2 | | | | |
| L6PK | 6.0 | 1.5 | 42.8 | 2.4 | 4.0 | 1.2 | 28.2 | 2.3 | | | | |
| WA3 | 5.9 | 1.4 | 47.1 | 2.7 | 3.5 | 1.1 | 29.1 | 2.2 | | | | |
| WA6 | 6.0 | 1.5 | 47.2 | 2.6 | 3.8 | 1.1 | 30.4 | 2.2 | | | | |
| WA12 | 5.4 | 1.3 | 47.7 | 3.5 | 3.6 | 1.1 | 32.4 | 2.4 | | | | |
| WA6P | 5.6 | 1.4 | 43.6 | 2.5 | 3.8 | 1.0 | 28.5 | 2.2 | | | | |
| LSD | 0.7 | 0.2 | 3.1 | 0.3 | 0.4 | 0.1 | 4.3 | 0.2 | | | | |

Table 6. Soil test values in field soils after cropping for three years.

| Treatment | Field experiment 1 in loamy clay | | | | | Field experiment 2 in clayey mull | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | pH($H_2O$) | Ca | Mg | K | P | pH($H_2O$) | Ca | Mg | K | P |
| Control | 6.3 | 2 170 | 430 | 181 | 12.8 | 5.5 | 2 910 | 265 | 124 | 5.5 |
| P | 6.3 | 2 340 | 436 | 179 | 21.1 | 5.4 | 2 980 | 261 | 125 | 6.5 |
| K | 6.3 | 2 250 | 439 | 191 | 16.3 | 5.4 | 2 880 | 263 | 150 | 5.4 |
| PK | 6.3 | 2 290 | 426 | 190 | 19.6 | 5.4 | 3 030 | 263 | 135 | 6.8 |
| L6PK | 6.5 | 2 460 | 463 | 196 | 20.2 | 5.6 | 3 270 | 343 | 131 | 7.2 |
| WA3 | 6.5 | 2 380 | 438 | 191 | 19.5 | 5.5 | 3 170 | 306 | 155 | 6.1 |
| WA6 | 6.7 | 2 580 | 448 | 203 | 25.1 | 5.7 | 3 360 | 326 | 206 | 6.4 |
| WA12 | 7.0 | 2 910 | 454 | 234 | 38.2 | 5.8 | 3 510 | 329 | 256 | 7.5 |
| WA6P | — | — | — | — | — | 5.6 | 3 350 | 311 | 168 | 9.3 |
| LSD | 0.2 | 200 | 84 | 18 | 7.0 | 0.2 | 340 | 39 | 42 | 1.4 |

ash. In the mull field, where P fertilization greatly improved growth, the P contents of young plants were not increased by ash or P fertilizer applications, because the nutrients were diluted in larger amounts of plant dry matter after the stimulated growth. In the clay field the contents of P in barley tissue were significantly increased by wood ash in the second and third years.

The pH of the field soils was increased more effectively by wood ash than by dolomitic limestone. The difference between these materials was significant in the determinations carried out in the first year (results unpublished). Both of these agents were approximately equal sources of extractable soil Ca (Table 6). The content of extraxtable Mg was not significantly increased by either agent in the clay soil, whereas both improved the status of this nutrient in the more acid mull soil. The increases in the contents of extractable K were significant in both soils, but much smaller in the clay.

The soil P test values differed only slightly in the mull field, while in the clay field P status was efficiently improved by wood ash application. This agreed with the increased contents of P measured in the barley grown in the plots treated with large rates of ash.

## DISCUSSION

### Neutralization capacity

The capacity of a liming agent to neutralize soil acidity depends on its content of such soluble and hydrolyzable bases as oxides, hydroxides, carbonates and silicates. Cations such ash calcium, magnesium and potassium are inactive counterions. Ashes may also contain heavier metals like aluminium and iron that form amphoteric oxides or hydroxides, which can react as acids or as bases, depending on their forms and soil pH. Both iron and manganese increase acidity when their reduced forms are oxidized and hydrolyzed to solid compounds. The formation of the soluble oxyanions nitrate and sulphate from ammonium and sulphide also generates acidity. Even the organic residues in ashes may be involved in the neutralization reactions in soils.

In the official quality control of liming materials in Finland, neutralization capacity is deter-

mined according to the contents of calcium and magnesium. This method is evidently less reliable for ashes, which have much more complex and variable compositions. The wood ashes 2 and 7, in which potassium was a major counterion, exerted greater efficiency in the titration procedure. Ashes can contain neutral salts such as sulphates and chlorides which do not neutralize soil acidity. These errors can be avoided by using the acid-base titration procedure.

Another source of error in the chemical determination of neutralization capacity is the sulphide sulphur, which is evaporated or remains inactive during the laboratory procedure, but is microbiologically oxidized to sulphuric acid in soil amended with ash. The smaller increase in soil pH and the large electrical conductivity in the soil treated with the peat ash 9 was probably largely due to sulphur compounds.

The wood ashes which contained soluble strong bases reacted quickly, but the completely burnt industrial bark ashes were not faster acting than the standard ground calcitic limestone. The low pH values of the peat ashes indicated that these materials did not contain any strong bases. The relative efficiency of the coal ash increased with decreasing pH. This probably resulted from the buffering effect of the oxihydroxides of aluminium and iron which may occur in large amounts in peat and coal ashes (ADRIANO et al. 1980).

The neutralizing effects obtained with the ashes of wood, bark and coal agreed with earlier studies, but peat ashes appeared to be less efficient than expected (JOKINEN 1982, HAKKILA and KALAJA 1983, AITKEN et al. 1984). The chemical determination of neutralization capacity seemed to be useful for predicting the highly varying efficiencies of ashes, even though the method was not very accurate for the poorer ashes.

## Nutrient availability

Calcium was the most abundant element of the four macronutrients in all of the other analyzed samples, but a straw ash contained many times more K than Ca. According to the chemical ash analyses, Ca is also released from ash more easily than Mg, K and P. However, additional studies (results unpublished) revealed that only a few per cent of the Ca, but nearly all the K extractable in citric acid, was soluble in water. Mg and P were released from the ashes by water even in smaller proportions than Ca. The fraction of Ca insoluble in diluted HCl was greatest in the peat ash samples, which is in accordance with earlier studies (JOKINEN 1982).

Despite of their relative abundance of Ca, large amounts of ashes did not ensure sufficient uptakes of this nutrient. The main reasons for this adverse effect seemed to be the high relative Mg content in coal ash and the excessive amounts of K in straw and wood ashes. The antagonistic effect by K on Ca uptake was strong on the pot-grown plants in peat soil. The higher Ca uptake of rye grass after the KCl application compared to the additions of $K_2SO_4$ and $K_2CO_3$ suggested that Ca uptake rate was increased by chloride ions, which are not abundant in ashes. The sulphate and carbonate anions may also form sparingly soluble calcium salts. The bark ash pellets did not dissolve in the soil but hardened like mortar due to the formation of calcium carbonate. The extremely low Ca contents of plants grown in the alkaline peat treated with large rates of wood ash suggested that even soluble Ca was captured by carbonate ions.

The ashes studied contained sufficient amounts of Mg to largely compensate for the antagonistic effect of excess K. They thus differ from such commercial K fertilizers as KCl which may substantially decrease the contents of Mg in plants grown in soils that are weakly buffered for K (SAARELA 1983). The Mg fraction that remained insoluble in soil was sizeable in peat ash, as also found earlier (JOKINEN 1982), but quite small in the other ashes.

The K contents of different ashes were ex-

tremely variable. The sizes of the available fractions of this nutrient varied relatively more than the total amounts because the poorer ashes contained more insoluble minerals. Straw ash was quite a concentrated K fertilizer. Wood ashes were also so abundant in K that large rates should be applied with caution to avoid the possible harmful effects of excess K. Some recent results obtained with red clover by HUOKUNA et al. (1988) suggested that even bark ashes may cause an excess of this nutrient. Coal and peat ashes are usually very poor in available K, but the amounts are not always totally negligible (MARTENS et al. 1970, KATZUR and GORA 1986).

In the field experiment on clay soil, wood ash proved inferior to the KCl fertilizer for barley grain production (SAARELA 1989). This difference seemed to be partly caused by a beneficial effect by the chloride in the fertilizer salt which had been placed in rows. Plant and soil analyses also showed that the wood ash rich in K was rather inefficient for increasing the contents of this nutrient in plants. Roughly 90 per cent of the water soluble K applied in the ash was fixed to the clay in forms inextractable in acid ammonium acetate. The fixation was probably not caused by the ash, but resulted from the store application of large rates of K in the ash in the K fixing clay. Finnish soils contain micaceous clay minerals that can fix large amounts of K (SIPPOLA 1974). The present results obtained under field conditions substantiated the importance of K fixing in Finnish clay soils, and are in agreement with earlier laboratory studies (KAILA 1965).

Coal ashes are usually very poor sources of P (ADRIANO et al. 1980, KATZUR and GORA 1986). Other ashes contain substantial amounts of this element in sparingly soluble compounds (SHUTT 1925, HARTIKAINEN 1984). According to the present study, the availability of the P applied in ashes is dependent on soil conditions. Ashes appeared to supply this nutrient rather efficiently in acid peat soils. The good efficacy obtained by wood ash in fertile clay soil was probably partly a result of the increased pH which is known to desorb P in Finnish soils (HARTIKAINEN 1981). In additional pot experiments in a clay soil (unpublished results) P availability to plants was enhanced more by wood and bark ashes than by peat ashes. The most important reason for this difference evidently was the higher contents of aluminium and iron in peat ashes.

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*Manuscript received November 1990*

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## SELOSTUS

# Puun, kuoren, turpeen ja kivihiilen tuhkat kalkitusaineina sekä kalsiumin, magnesiumin, kaliumin ja fosforin lähteinä

INTO SAARELA

Maatalouden tutkimuskeskus

Erilaisia tuhkia tutkittiin kalkitus- ja lannoitusaineina astia- ja kenttäkokein vuosina 1980—1986. Kemiallisesti määritettyä maan happamuutta neutraloivaa vaikutusta ja erilaisiin uuttoliuoksiin liukenevia ravinnefraktioita verrattiin tuhkien vaikutukseen maan pH-lukuun ja ravinnetilaan sekä raiheinän, ohran ja kauran ravinteiden saantiin. Pienten lämpökeskusten puun tuhka oli tehokasta ja nopeasti vaikuttavaa kalkitusainetta, mutta suurissa määrissä puun tuhkaa maahan tuli kasvien tarpeeseen verrattuna ylimäärin kaliumia, joka vaikeutti kasvien kalsiumin ottoa varsinkin turvemailla. Enemmän palamatonta polttoainetta ja kosteutta sisältävät teollisuuden kuoren tuhkat olivat laimeampia kuin puun tuhkat. Fossiilisten polttoaineiden turpeen ja kivihiilen tuhkat olivat suhteellisen heikkotehoisia kalkitusaineita ja niukkaravinteisia. Kivihiilen tuhkassa oli kuitenkin liukoista magnesiumia kalsiumiin verrattuna niin runsaasti, että se suurina määrinä nosti kasvin magnesiumpitoisuuden normaalia suuremmaksi ja alensi kasvin kalsiumpitoisuutta. Tulosten mukaan tuhkien kalkitusvaikutus voidaan arvioida luotettavimmin happo-emästitraukseen perustuvalla menetelmällä ja lannoitusvaikutus voidaan ennakoida tarkimmin ravinteiden liukoisuuden huomioon ottavalla määrityksellä, kuten laimealla sitruunahapolla uuttamalla.

Appendix 1. Total amounts of nutrients applied in lime or ashes and fertilizers as well as total dry matter yield and nutrient uptake of rye grass in four cuts in pot experiment P1 with nutrient balances (= applied-uptake) and soil data for some selected treatments. Nutrients given in mg per liter of soil.

| Treatment | Lime or ash g/l of soil | Applied in lime or ash (A) and fertilizer (F) | | | | Yield g/l soil | Nutrient uptake by rye grass* | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Calcium A/F | Magnesium A/F | Potassium A/F | Phosphorus A/F | | Calcium | Magnesium | Potassium | Phosphorus |
| L0 | — | 0/ 50 | 0/ 40 | 0/400 | 0/80 | 11.4 | 30 | 27 | 428 | 34 |
| L1 | 3 gr. limest. | 1 020/ 50 | 5/ 40 | 3/400 | 1/80 | 13.6 | 150 | 56 | 414 | 57 |
| L2 | 6 gr. limest. | 2 040/ 50 | 10/ 40 | 6/400 | 2/80 | 14.7 | 186 | 60 | 416 | 58 |
| P0 | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/400 | 0/ 0 | 5.7 | 38 | $8^{c}$ | 264 | $8^{a}$ |
| P1 | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/400 | 0/40 | 12.7 | 136 | 50 | 405 | 31 |
| P2K2 | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/400 | 0/80 | 14.0 | 172 | 57 | 414 | 58 |
| K0 | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/ 0 | 0/80 | 1.1 | $6^{a}$ | $2^{a}$ | $6^{a}$ | $8^{a}$ |
| K1 | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/200 | 0/80 | 8.6 | 92 | 32 | 215 | 44 |
| K2, 5 | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/500 | 0/80 | 17.0 | 198 | 56 | 471 | 55 |
| K2Cl | 3.6 $CaCO_3$ | 1 440/153 | 0/102 | 0/400 | 0/80 | 15.1 | 200 | 82 | 412 | 57 |
| $K2SO_4$ | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/400 | 0/80 | 14.2 | 124 | 40 | 407 | 58 |
| $K2CO_3$ | 3.6 $CaCO_3$ | 1 440/ 50 | 0/ 40 | 0/400 | 0/80 | 12.9 | 139 | 44 | 391 | 58 |
| SA10 | 2 straw ash | 64/ 0 | 14/ 0 | 480/ 0 | 23/ 0 | 9.9 | $23^{d}$ | $17^{c}$ | 496 | $17^{c}$ |
| SA10P | 2 straw ash | 64/ 25 | 14/ 0 | 480/ 0 | 23/40 | 10.5 | $27^{e}$ | 20 | 498 | 38 |
| SA20 | 4 straw ash | 128/ 0 | 28/ 0 | 960/ 0 | 47/ 0 | 16.2 | 33 | 23 | 859 | 37 |
| SA20P | 4 straw ash | 128/ 25 | 28/ 0 | 960/ 0 | 47/40 | 18.2 | 37 | 26 | 950 | 60 |
| WA10 | 2 wood ash | 504/ 0 | 85/ 0 | 232/ 0 | 35/ 0 | 7.3 | 44 | 22 | 266 | 26 |
| WA10P | 2 wood ash | 504/ 25 | 85/ 0 | 232/ 0 | 35/40 | 7.9 | 47 | 28 | 258 | 43 |
| WA20 | 4 wood ash | 1 008/ 0 | 170/ 0 | 465/ 0 | 71/ 0 | 12.9 | 70 | 34 | 504 | 36 |
| WA20P | 4 wood ash | 1 008/ 25 | 170/ 0 | 465/ 0 | 71/40 | 13.5 | 75 | 43 | 505 | 40 |
| BA20 | 4 bark ash | 756/ 0 | 66/ 0 | 138/ 0 | 33/ 0 | 3.8 | $28^{e}$ | $10^{c}$ | $48^{d}$ | $15^{b}$ |
| BA20PK | 4 bark ash | 756/ 25 | 66/ 0 | 138/100 | 33/40 | 6.5 | 53 | 26 | $148^{g}$ | 32 |
| BA40 | 8 bark ash | 1 512/ 0 | 131/ 0 | 277/ 0 | 66/ 0 | 6.1 | 59 | $17^{e}$ | $76^{e}$ | $19^{d}$ |
| BA40PK | 8 bark ash | 1 512/ 25 | 131/ 0 | 277/100 | 66/40 | 9.1 | 88 | 38 | $175^{h}$ | 40 |
| PA80 | 16 peat ash | 640/ 0 | 93/ 0 | 197/ 0 | 178/ 0 | 2.0 | $11^{b}$ | $6^{b}$ | $17^{b}$ | $14^{b}$ |
| PA80PK | 16 peat ash | 640/ 25 | 93/ 0 | 197/100 | 178/40 | 5.1 | $24^{d}$ | $13^{d}$ | $120^{f}$ | 32 |
| PA160 | 32 peat ash | 1 280/ 0 | 186/ 0 | 394/ 0 | 355/ 0 | 2.8 | $17^{c}$ | $9^{c}$ | $29^{c}$ | $21^{e}$ |
| PA160PK | 32 peat ash | 1 280/ 25 | 186/ 0 | 394/100 | 355/40 | 5.8 | 38 | $19^{e}$ | $129^{f}$ | 42 |
| LSD | | | | | | 0.9 | 12 | 5 | 62 | 3 |

| Treatment | Balance of nutrients | | | | In soil after experiment** | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Ca | Mg | K | P | pH($H_2O$) | Ca | Mg | K | P |
| K0 | 1 484 | 38 | −6 | 72 | $4.0^{a}$ | $1\,350^{c}$ | $108^{c}$ | $20^{a}$ | $21^{c}$ |
| P2K2 | 1 318 | −17 | −14 | 22 | $5.0^{c}$ | $1\,710^{e}$ | $24^{a}$ | $30^{ab}$ | $5^{a}$ |
| SA20 | 95 | 5 | 101 | 10 | $4.2^{a}$ | $530^{a}$ | $48^{b}$ | $175^{c}$ | $3^{a}$ |
| WA20 | 938 | 136 | −39 | 35 | $4.8^{bc}$ | $1\,460^{cd}$ | $250^{e}$ | $40^{b}$ | $8^{b}$ |
| BA40 | 1 453 | 72 | 201 | 47 | $4.7^{b}$ | $1\,580^{d}$ | $156^{d}$ | $20^{a}$ | $5^{a}$ |
| BA160 | 1 263 | 169 | 365 | 334 | $4.2^{a}$ | $930^{b}$ | $125^{cd}$ | $21^{a}$ | $23^{c}$ |

* Values followed by different letters differ according to pairwise t-tests ($p = 0.05$)
** Values not followed by the same letter differ significantly (Duncan 0.05)

Appendix 2. Total amounts of nutrients applied in lime or ashes (A) and in fertilizers (F) as well as nutrient contents and uptakes in plants as well as balances and extractable contents in soil after cropping for three years in the pot experiment P2.

| Treatment | Applied g/l soil A/F | Content of barley, 1st year (g/kg) | | | Uptake (mg/l of soil) | | Balance mg/l soil | In soil mg/l |
|---|---|---|---|---|---|---|---|---|
| | | Sprouts | Straw | Grain | 1st year | years 1—3 | | |
| | | | | Calcium | | | | |
| L1F1 | 1 630/ 0 | 10.6 | 19.4 | 0.46 | 202 | 434 | 1 196 | 1 880 |
| A1WA2 | 1 058/ 0 | 6.1 | 15.1 | 0.33 | 170 | 320 | 738 | 1 240 |
| A1PA4 | 2 000/ 0 | 0.5 | 24.9 | 0.54 | 233 | 478 | 1 522 | 1 810 |
| A1BA5 | 1 296/ 0 | 8.8 | 19.6 | 0.47 | 198 | 380 | 916 | 1 350 |
| A1CA6 | 905/ 0 | 4.9 | 14.0 | 0.33 | 129 | 262 | 643 | 1 030 |
| L2F1 | 3 220/ 0 | 12.0 | 21.8 | 0.44 | 189 | 434 | 2 786 | 3 810 |
| L2F2 | 3 220/ 0 | 10.4 | 18.4 | 0.42 | 221 | 481 | 2 739 | 3 690 |
| A2WA2 | 2 116/ 0 | 6.9 | 10.6 | 0.29 | 118 | 282 | 1 834 | 2 130 |
| A2BA3 | 2 646/ 0 | 9.4 | 17.7 | 0.33 | 200 | 407 | 2 239 | 2 550 |
| A2BA3P | 2 646/ 0 | 9.6 | 17.7 | 0.36 | 219 | 482 | 2 164 | 2 340 |
| A2BA5 | 2 592/ 0 | 10.3 | 16.3 | 0.38 | 197 | 366 | 2 226 | 2 360 |
| A2CA6 | 1 810/ 0 | 4.5 | 12.4 | 0.30 | 110 | 254 | 1 556 | 1 430 |
| A2CA6P | 1 810/ 0 | 5.1 | 12.5 | 0.36 | 120 | 286 | 1 524 | 1 330 |
| LSD | | 1.3 | 2.4 | 0.06 | 25 | 40 | | 240 |
| | | | | Magnesium | | | | |
| L1F1 | 7/ 40 | 1.3 | 2.3 | 1.2 | 31 | 100 | −13 | 70 |
| A1WA2 | 178/ 0 | 1.7 | 2.8 | 1.5 | 39 | 120 | 98 | 191 |
| A1PA4 | 81/ 40 | 1.1 | 2.8 | 1.3 | 32 | 105 | 86 | 46 |
| A1BA5 | 106/ 0 | 1.3 | 2.5 | 1.5 | 31 | 100 | 46 | 79 |
| A1CA6 | 428/ 0 | 2.8 | 6.1 | 1.7 | 63 | 172 | 296 | 359 |
| L2F1 | 14/ 40 | 1.2 | 3.1 | 1.3 | 33 | 103 | − 7 | 106 |
| L2F2 | 14/ 80 | 1.2 | 2.4 | 1.4 | 38 | 118 | 16 | 149 |
| A2WA2 | 356/ 0 | 2.1 | 1.9 | 1.4 | 29 | 102 | 294 | 463 |
| A2BA3 | 230/ 0 | 1.3 | 2.7 | 1.3 | 39 | 117 | 153 | 226 |
| A2BA3P | 230/ 0 | 1.4 | 2.4 | 1.3 | 40 | 133 | 137 | 184 |
| A2BA5 | 211/ 0 | 1.5 | 2.1 | 1.3 | 35 | 99 | 152 | 204 |
| A2CA6 | 856/ 0 | 2.9 | 7.5 | 1.6 | 74 | 197 | 699 | 660 |
| A2CA6P | 856/ 0 | 3.4 | 7.9 | 1.8 | 82 | 227 | 669 | 604 |
| LSD | | 0.2 | 0.8 | 0.1 | 8 | 15 | | 21 |
| | | | | Potassium | | | | |
| L1F1 | 4/200 | 57 | 11.7 | 8.6 | 173 | 654 | 150 | 64 |
| A1WA2 | 488/ 0 | 77 | 28.8 | 8.8 | 369 | 894 | 194 | 38 |
| A1PA4 | 172/200 | 70 | 15.9 | 9.6 | 193 | 665 | 307 | 68 |
| A1BA5 | 139/200 | 70 | 22.2 | 9.4 | 257 | 703 | 236 | 53 |
| A1CA6 | 703/200 | 64 | 15.9 | 9.5 | 181 | 678 | 825 | 66 |
| L2F1 | 8/200 | 63 | 15.6 | 8.9 | 178 | 621 | 181 | 100 |
| L2F2 | 8/400 | 73 | 21.8 | 8.6 | 318 | 819 | 189 | 108 |
| A2WA2 | 976/ 0 | 82 | 52.3 | 8.5 | 623 | 1 400 | 176 | 173 |
| A2BA3 | 484/200 | 71 | 21.4 | 7.2 | 291 | 834 | 450 | 93 |
| A2BA3P | 484/200 | 68 | 17.4 | 8.0 | 275 | 824 | 460 | 106 |
| A2BA5 | 278/200 | 67 | 28.4 | 7.5 | 397 | 884 | 194 | 155 |
| A2CA6 | 1 406/200 | 68 | 17.6 | 9.0 | 197 | 692 | 1 514 | 72 |
| A2CA6P | 1 406/200 | 64 | 16.1 | 10.3 | 192 | 665 | 1 541 | 88 |
| LSD | | 6 | 3.5 | 0.9 | 36 | 61 | | 26 |
| | | | | Phosphorus | | | | |
| L1F1 | 1/ 40 | 4.2 | 0.8 | 3.2 | 27 | 86 | 35 | 4.7 |
| A1WA2 | 74/ 40 | 6.1 | 3.1 | 5.5 | 64 | 129 | 65 | 8.9 |
| A1PA4 | 155/ 0 | 3.8 | 1.2 | 3.9 | 30 | 103 | 132 | 6.5 |
| A1BA5 | 48/ 40 | 5.2 | 2.5 | 5.5 | 46 | 98 | 70 | 8.5 |
| A1CA6 | 42/ 40 | 4.7 | 1.7 | 4.9 | 35 | 93 | 69 | 5.0 |
| L2F1 | 2/ 40 | 3.9 | 1.0 | 3.2 | 24 | 86 | 36 | 5.0 |
| L2F2 | 2/ 80 | 4.9 | 1.4 | 4.5 | 48 | 121 | 41 | 5.5 |
| A2WA2 | 149/ 20 | 4.8 | 1.5 | 4.8 | 45 | 124 | 125 | 15.2 |
| A2BA3 | 116/ 0 | 3.8 | 0.7 | 3.1 | 31 | 102 | 94 | 6.1 |
| A2BA3P | 116/ 40 | 5.0 | 1.3 | 4.4 | 50 | 129 | 107 | 6.9 |
| A2BA5 | 96/ 20 | 4.4 | 0.8 | 3.8 | 41 | 118 | 78 | 8.1 |
| A2CA6 | 84/ 0 | 3.7 | 0.8 | 3.6 | 24 | 86 | 78 | 3.9 |
| A2CA6P | 84/ 40 | 5.2 | 1.9 | 4.9 | 37 | 104 | 100 | 4.4 |
| LSD | | 0.8 | 0.8 | 0.4 | 9 | 12 | | 1.2 |

Appendix 3. Nutrient application as well as contents (g/kg) and uptakes (mg/l of soil) of plants with nutrient balances and extractable contents in soils after cropping for two years in the pot experiment P3.

| Treatment | Nutrients annually mg/l of soil in lime or ash/fertil. | Oats 1982 | | | Barley 1983 | | | 1982 + 1983 uptake mg/l soil | Nutrient balance mg/l soil | Extractable in soil mg/l | Oats 1984 uptake mg/l soil |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | grain g/kg | straw g/kg | uptake mg/l soil | grain g/kg | straw g/kg | uptake mg/l soil | | | | |
| | | | | | Calcium | | | | | | |
| L1 | 1 208/ — | 0.82 | 7.2 | 88 | 0.41 | 9.9 | 94 | 181 | 2 235 | 7 500 | 127 |
| L2 | 2 415/ — | 0.74 | 5.8 | 102 | 0.50 | 9.7 | 106 | 208 | 4 622 | 11 560 | 154 |
| WA1 | 767/ — | 0.68 | 6.0 | 89 | 0.28 | 7.4 | 73 | 161 | 1 373 | 4 910 | 65 |
| WA2 | 1 534/ — | 0.68 | 4.7 | 73 | 0.33 | 7.8 | 88 | 161 | 2 907 | 8 060 | 57 |
| BA2 | 1 706/ — | 1.02 | 6.8 | 121 | 0.33 | 10.4 | 104 | 225 | 3 187 | 9 060 | 110 |
| PA2 | 2 952/ — | 0.81 | 7.3 | 108 | 0.41 | 9.3 | 105 | 212 | 5 692 | 5 160 | 112 |
| LSD | | 0.20 | 0.7 | 13 | 0.04 | 1.4 | 16 | 17 | | 1 380 | 18 |
| | | | | | Magnesium | | | | | | |
| L1 | 6/ —* | 1.3 | 3.8 | 53 | 1.3 | 2.7 | 37 | 90 | −78 | 674 | 49 |
| L2 | 12/ —* | 1.5 | 3.1 | 58 | 1.4 | 1.9 | 38 | 96 | −72 | 679 | 50 |
| WA1 | 116/ —* | 1.5 | 3.5 | 60 | 1.4 | 2.2 | 35 | 95 | 138 | 830 | 27 |
| WA2 | 233/ — | 1.4 | 2.3 | 45 | 1.5 | 2.0 | 38 | 83 | 382 | 1 180 | 34 |
| BA2 | 203/ — | 1.7 | 3.3 | 64 | 1.5 | 2.8 | 42 | 106 | 300 | 885 | 42 |
| PA2 | 490/ — | 1.6 | 3.4 | 61 | 1.5 | 2.8 | 49 | 110 | 870 | 558 | 44 |
| LSD | | 0.2 | 0.3 | 7 | 0.1 | 0.3 | 3 | 7 | | 126 | 8 |
| | | | | | Potassium | | | | | | |
| L1 | 3/200* | 4.8 | 13.8 | 190 | 7.1 | 16.5 | 224 | 415 | −9 | 45 | 351 |
| L2 | 6/400* | 5.2 | 23.5 | 380 | 7.2 | 23.0 | 334 | 714 | 98 | 175 | 379 |
| WA1 | 310/ — | 5.0 | 18.9 | 303 | 6.4 | 23.5 | 286 | 589 | 31 | 158 | 392 |
| WA2 | 620/ — | 5.3 | 43.4 | 665 | 6.6 | 36.8 | 469 | 1 134 | 106 | 390 | 616 |
| BA2 | 370/ — | 4.7 | 14.8 | 277 | 6.6 | 16.5 | 225 | 500 | 240 | 141 | 295 |
| PA2 | 428/100** | 4.9 | 10.5 | 186 | 6.9 | 9.5 | 185 | 372 | 684 | 50 | 304 |
| LSD | | 0.3 | 2.0 | 58 | 0.3 | 2.5 | 42 | 66 | | 42 | 77 |
| | | | | | Phosphorus | | | | | | |
| L1 | 1/ 30* | 2.5 | 0.14 | 20 | 2.1 | 0.36 | 25 | 44 | 18 | 5.4 | 63 |
| L2 | 2/ 60* | 4.3 | 0.51 | 50 | 3.2 | 0.37 | 47 | 97 | 27 | 17.6 | 61 |
| WA1 | 63/ — | 4.0 | 0.22 | 38 | 2.4 | 0.34 | 27 | 65 | 61 | 28.5 | 19 |
| WA2 | 126/ — | 3.8 | 0.19 | 37 | 3.0 | 0.41 | 36 | 73 | 179 | 98.0 | 32 |
| BA2 | 97/ — | 4.4 | 0.71 | 29 | 2.9 | 0.37 | 32 | 61 | 133 | 55.5 | 28 |
| PA2 | 446/ — | 4.7 | 2.04 | 69 | 3.9 | 0.62 | 55 | 124 | 768 | 35.7 | 44 |
| LSD | | 0.4 | 0.16 | 3 | 0.3 | 0.11 | 2 | 3 | | 1.9 | 4 |

* In 1984 40 mg Mg, 300 mg K and 80 mg P per liter of soil
** 200 in 1984

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 389—405 (1991)
Seria AGROGEOLOGIA ET -CHIMICA N. 165 — Sarja MAA JA LANNOITUS n:o 165

# BORON DEFICIENCY IN BARLEY

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SIMOJOKI, P. 1991. **Boron deficiency in barley**. Ann. Agric. Fenn. 30: 389—405. (Agric. Res. Centre of Finland, Central Finland Res. Sta. SF-41340 Laukaa, Finland.)

Open-flower-sterility-ergot syndrome in barley was studied with field experiments in farms. The syndrome turned out to be a consequence of boron deficiency. The flower was opened by the swelling ovary. The swelling of the ovary was due in turn to partial pollen sterility caused by the boron deficiency. More than 80 % of the flowers may have been sterile. Liming had no effect on boron deficiency in these one-year experiments. Fertility recurred and the grain yield rose to the normal level with 350—600 g/ha of boron applied in cultivation of the soil or as foliar spray. There was already an obvious decrease in sterility with 160—300 g/ha of boron. In areas where boron fertilization had an obvious effect on the sterility of the barley, only 0.05—0.2 mg/l of hot water extractable boron was found in the soil. The leaves of sprouts at the 4—5 leaf stage contained about 3 mg/kg dry matter (DM) of boron. The appearance of the deficiency as sterility could not be predicted on the basis of the content of boron in the sprouts. The lateral and the adventitious shoots were more sterile than the main shoots. In the very same way boron fertilization affected the sterility of the six-rowed and two-rowed cultivars.

The boron deficiency of barley was connected with the appearance of ergot. When no pollination occurred the ovary began to swell and opened the flower of barley. Thus the infection of the ergot fungus (*Claviceps purpurea* (Fr.) TUL) was possible. The abundant pollen sterility and open flower were generally followed by a large number of ergot. Thus the most ergot sclerotia were often found in the adventitious shoots. This was also influenced by the abundance of the secondary contamination when the flowers of the adventitious shoots opened. The possibility of exploiting the pollen sterility of barley in ergot cultivation was noted.

Boron fertilization increased the content of water-soluble boron in the soil by 0.02 mg/l per 100 g/ha of applied boron. Symptoms of boron toxicity in barley were noted when the content of water-soluble boron in the soil exceeded 0.8 mg/l. The boron content in the leaves of barley at the heading stage rose on an average by 0.6 mg/kg DM per 100 g/ha of boron applied by broadcast fertilization. Boron applied by the placement method in the granules of (NPK) compound fertilizer raised the boron content of the leaves by 2 mg/kg DM per 100 g/ha of boron. The boron contents in the leaves of the cereals were on average only a fifth of the contents of dicotyledonous plants (shoots of pea, potato and lettuce). In the soil, 1.5 % of the total boron was hot water soluble. A suitable content of soluble boron in the soil may be 0.3—0.7 mg/l, in the cultivation of barley, and the content of boron in the leaves of barley at the heading stage 6—20 mg/kg DM.

Index words: boron, boron deficiency, barley, pollen sterility, ergot, *Claviceps purpurea*, boron fertilization, soil boron, water soluble boron, boron uptake, boron content, boron toxic symptoms.

## INTRODUCTION

From various parts of Finland there have been reports about shrivelled heads and ergot in barley since the mid 1960s. The ergot was the main cause of concern and also of preliminary research. The connection between shrivelled heads, ergot symptoms and sterility was soon noted. The sterility of barley could already be observed at the stage when the ear appeared from the ocrea. Pale colouring and transparency distinguished the sterile spikelets from the fertile ones. This pale colouring was caused by the fact that the sheltering leaves of the non-fertile flowers were open, thereby allowing daylight to gleam trough the spikelets. Even the awns were directed slightly sidewise. The open flower was often attacked by the ergot fungus. The open-flower stage lasted a couple of weeks. In the autumn the ears frequently contained both grains and empty spikelets, and ergots as well. Although the barley plant stand was generally luxuriant, the grain harvest could remain very small.

Starting in 1965, and particularly in 1968—1973, many field experiments were performed in Finland to determine the dependence of the sterility-ergot syndrome in barley on the supply of boron. Many boron fertilization tests also indicated the effect of boron fertilization on the boron content of the soil and of the plant. On the basis of the boron content efforts were made to predict the appearance of boron deficiency in the grain harvest. The boron content in pea, potato and lettuce was also studied.

## MATERIAL AND METHODS

The research comprised field experiments on arable land where ergot symptoms or boron deficiency had been noted. Most of this arable land was situated in the vicinity of the Central Finland Research Station. The experiments were generally carried out either in sandy or humus soil where the content of hot water extractable boron (HWB) in the soil was 0.05—0.2 mg/l. Although the experiments were made in suspected deficiency areas, deficiency symptoms in barley were not observed in all of them. Moreover the experimental material for this report was mainly chosen where sterility appeared. This illuminates the cause and effect relationship between sterility and the supply of boron. The experiments used randomized blocks; the split-plot design was used in the multifactor experiments. The significances of the differences in the means were tested with the analysis of variance.

Boron fertilization was carried out in most of the field experiments. The boron fertilizers were mainly borax, which contains 11.3 % boron, fertilizer borate (14.0 %) and soluboron (20.5 %). The sterility of the barley spikelets was determined by examining 20—50 ripe ears taken from each plot in the field experiments. A grainless spikelet was regarded as sterile, as was a spikelet with ergot. Ears with a maximum of three grains were classified as sterile ears. Ergot appeared in only some of the field experiments. Its abundance was determined from 20—40 ears in each experiment plot. The yield of ergot sclerotia was also determined for some experiments.

The amount of boron soluble in hot water (mg/l) was determined from the soil in some samples, as was the total boron from $Na_2CO_3$-melt. The boron content in the plant (mg/kg DM) was often determined from the leaves of

barley at the heading stage, and often from the sprouts at the 4—5 leaf stage as well. The boron determinations were made at the Soil Science Section of the Agricultural Research Centre and at Viljavuuspalvelu Co Ltd.

## RESULTS

### Boron deficiency and the sterility of barley

Table 1 contains 20 experiments where sterility appeared and in which boron had a significant effect on it. The experiments have been described in greater detail in earlier publications (SIMOJOKI 1969, 1972, 1988). The biggest proportion of sterile spikelets was 81 %. In three of the experiments the boron caused a decrease in sterility of more than 40 percentage points. In these 20 experiments, sterile spikelets averaged 40 % in the control treatment and 18 % in the boron treatment. The smallest boron amount which significantly reduced sterility was 160 g/ha. In seven experiments the boron content in the leaves of both the sprouts and those at the heading stage was determined in addition to the sterility. Boron fertilization (on average 470 g/ha) reduced the sterility from 45 % to 19 %. It also increased the boron content in the sprouts from 3.74 mg to 4.75 mg/kg DM and the boron content in the leaves at the heading stage from 2.89 mg to 5.11 mg/kg DM. Although the contents were of the same order in many other experiments, barley was fertile.

In most of the experiments boron fertilizer was applied, either borax 5 kg/ha as foliar spray or 10 kg/ha of fertilizer borate in connection with cultivation of the soil. The amounts were rather large and the effect was obvious. The results of two experiments are presented as ex-

Table 1. The effect of boron fertilization (B) on the sterility of barley in 20 field experiments in 1965—72.

| Year | Soil | pH | HWB mg/l | Sterile spikelets % | | LSD t 0.05 | Boron fert. g/ha |
|---|---|---|---|---|---|---|---|
| | | | | 0 | B | | |
| 1965 | peat | 5.9 | 0.10 | 52 | 9 | 18 | 1 400 |
| 1965 | sand | 5.6 | 0.20 | 57 | 12 | 19 | 1 400 |
| 1968 | sand | 5.7 | 0.15 | 42 | 11 | 15 | 1 400 |
| 1969 | sand | 6.4 | 0.10 | 35 | 11 | 10 | 340 |
| 1969 | sand | 6.2 | 0.15 | 34 | 16 | 6 | 1 400 |
| 1969 | sand | 6.2 | 0.15 | 24 | 5 | 9 | 1 400 |
| 1969 | fine sand | 6.1 | 0.17 | 27 | 19 | 4 | 1 400 |
| 1969 | fine sand | 6.1 | 0.17 | 12 | 6 | 3 | 1 400 |
| 1969 | sand | 6.4 | 0.10 | 49 | 28 | 15 | 1 400 |
| 1969 | sand | 6.4 | 0.10 | 34 | 12 | 18 | 350 |
| 1969 | humus | 6.4 | 0.07 | 41 | 25 | 14 | 1 400 |
| 1970 | fine sand | 6.1 | 0.16 | 20 | 13 | 4 | 1 400 |
| 1970 | humus | 5.4 | 0.14 | 37 | 13 | 17 | 565 |
| 1970 | humus | 5.4 | 0.14 | 12 | 7 | 4 | 565 |
| 1970 | humus | 5.4 | 0.10 | 62 | 37 | 0 | 565 |
| 1971 | humus | 5.5 | 0.08 | 60 | 31 | 12 | 600 |
| 1971 | humus | 5.5 | 0.08 | 81 | 35 | 23 | 160 |
| 1971 | humus | 5.4 | 0.08 | 53 | 26 | 26 | 900 |
| 1972 | humus | 5.0 | 0.11 | 28 | 17 | 7 | 1 025 |
| 1972 | humus | 5.0 | 0.11 | 38 | 29 | 5 | 300 |

Table 2. The effect of boron fertilization method on the sterility of barley in 1969. Fine sand, pH 6.4, B 0.1 mg/l. Borax was spread in connection with cultivation of the soil or sprayed on the sprouts at the 3-leaf stage.

| Boron g/ha | Sterile spikelets % | |
|---|---|---|
| | Boron into soil | Boron as foliar spray |
| 0 | 35 | |
| 339 | 13 | 13 |
| 678 | 14 | 14 |
| 1 356 | 11 | 9 |
| B-fertilization | ** | |
| method | n.s. | |

** $P<0.01$, n.s. = not significant ($P<0.05$)

Table 3. The effect of various boron doses on the sterility of barley and the boron content in three experiments in 1971. Boron was applied in connection with cultivation of the soil.

| Boron g/ha | Spikelet sterility % | Boron in the leaves mg/kg DM | HWB in the soil mg/l |
|---|---|---|---|
| 0 | 32[a] | 3.18[a] | 0.31[a] |
| 150 | 17[b] | 3.92[b] | 0.37[a] |
| 600 | 13[b] | 6.03[c] | 0.44[b] |

[a–c] Different letters in the same column indicate significance ($P<0.05$)

amples of the effects of the smaller amounts of boron and of the various practices of fertilization. Tables 2 and 3 show that 150—340 g/ha of boron is already enough to minimize sterility. With regard to the effect of boron, there were no differences between the two methods of spreading. The boron content in the leaves at the heading stage rose along with increased boron fertilization, although not in quite the same proportion. With 100 g/ha of applied boron, the boron content in the leaves rose on average by 0.3—0.7 mg/kg DM, and the content of water-soluble boron in the soil by 0.02—0.04 mg/l.

Liming had no effect on the sterility of barley in five one-year experiments (Table 4). The liming did not significantly increase or decrease the harvest in the 1970 liming experiment. On the other hand, boron fertilization reduced the sterility and increased the grain harvest. The most sterile spikelets were found in the adventitious shoots. Boron fertilization raised the boron content of the leaves.

There were fewer sterile spikelets in the two-rowed barley cultivars than in the six-rowed ones (Table 5). Boron fertilization increased the harvest and reduced the sterility and the ergot. The effect of boron on cultivars representing various types of ear was the same. The earliness of the cultivars obviously did not directly affect the occurrence of sterility. In the adventitious shoots there was abundant sterility in spite of the boron fertilization abundant sterility. In

Table 4. The effect of liming and boron fertilization on the harvest and the sterility of barley on humus soil in 1970 and on the sterility in five experiments in 1969—71. HWB in the soil 0.1 mg/l. Boron fertilization 5 kg/ha borax (1970) or 10 kg/ha fertilizer borate.

| Ground limestone t/ha | Boron | Experiment 1970 | | | Sterile spikelets % mean |
|---|---|---|---|---|---|
| | | Grain yield kg/ha | Sterile spikelets % | Boron in the leaves mg/kg DM | |
| 0 | 0 | 1 790 | 41 | 2.73 | 40 |
| 0 | B | 3 670 | 12 | 3.91 | 21 |
| 5 | 0 | 1 870 | 30 | 1.99 | 36 |
| 5 | B | 3 410 | 11 | 4.95 | 18 |
| F:liming | | n.s. | n.s. | n.s. | n.s. |
| B-fertilization | | * | *** | *** | *** |

* $P<0.05$, *** $P<0.001$, n.s. = not significant ($P<0.05$)

Table 5. Results of the effect of boron fertilization on the harvest and the sterility of two and six-rowed barley cultivars in two of the experiments in 1969. All the two-rowed were later than the six-rowed. Fertilizer borate (10 kg/ha) given in connection with cultivation. In the soil HWB 0.15 mg/l (0.55 mg/l on the boron plots).

| Ear type of cultivars | | kg/ha | Sterile spikelets % |
|---|---|---|---|
| Six rowed | 0 | 2 660 | 42 |
| | B | 3 250 | 15 |
| Two-rowed | 0 | 2 900 | 31 |
| | B | 3 590 | 4 |
| Mean | 0 | 2 780 | 36 |
| | B | 3 420 | 10 |
| F:B-fertilization | | *** | *** |
| rowiness | | n.s. | * |
| B × rowiness | | n.s. | n.s. |

* $P<0.05$, *** $P<0.001$, n.s. = not significant ($P<0.05$)

the two-rowed cultivars sterility was limited almost entirely to the lateral shoots and the adventitious shoots (Table 6).

Table 6. Results of the sterility of the barley ears in the cultivar experiment of 1970. In the soil HWB 0.19 mg/l (on the boron plots 0.44 mg/l). Boron fertilization 5 kg/ha borax as spray on the sprouts.

| Cultivar | Boron fertilization | Sterile ears %[1] | | |
|---|---|---|---|---|
| | | Main shoot | Lateral shoot | Adventitious shoot |
| Pirkka | 0 | 25 | 19 | 81 |
| | B | 0* | 1* | 21* |
| Etu | 0 | 1 | 17 | 50 |
| | B | 0* | 2* | 42 |
| Paavo | 0 | 15 | 19 | 89 |
| | B | 0* | 0* | 28*** |
| Mean (six-rowed) | 0 | 14 | 19 | 73 |
| | B | 0** | 1** | 30** |
| Mari | 0 | 0 | 10 | 61 |
| | B | 0 | 1** | 31** |
| Ingrid | 0 | 0 | 7 | 52 |
| | B | 0 | 0 | 12** |
| Birgitta | 0 | 2 | 17 | 80 |
| | B | 0** | 0** | 13** |
| Mean (two-rowed) | 0 | 1 | 11 | 64 |
| | B | 0 | 0* | 19*** |

[1] sterile ear = maximum 3 grains
Statistical significance 0 — B: * $P<0.05$, ** $P<0.01$, *** $P<0.001$

Sowing time had a definite effect on the sterility of barley in three sowing time experiments: the later the sowing, the greater the percentage of empty spikelets in the ears (Table 7). Boron fertilization was obviously favourable. However, it could not reduce the sterility of the late sowings to the level of the earlier sowing. The late sowings may have suffered from the drying of the soil.

In barley with an abundance of open flower the lodged corn may have affected the open-flower and shrivelled-head phenomenon. Some flattened corn experiments of an observational character were performed in 1980—81. Flattening of the crop with a metal thread net prior to ear formation increased sterility in the barley. In barley that was not laid flat 15 % of the spikelets were sterile and 30—50 % in the flattened corn. Boron fertilization did not reduce sterility in the flattened plots.

## Boron deficiency in barley and the amount of ergot

The yield of ergot sclerotia was determined from five experiments. The results (Table 8) showed that boron fertilization increased the barley harvest in these experiments by an average of 65 % and reduced the yield of ergot sclerotia from 53 kg/ha to 2 kg/ha. The proportion of sterile spikelets decreased at the same

Table 7. The influence of sowing time and boron fertilization on the sterility of barley in three experiments. Boron (565—1 400 g/ha) was applied in connection with cultivation of the soil. Sowing time intervals 4 days.

| Boron-fertilization | Sterile spikelets % in 1—3 sowings | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | mean |
| 0 | 31 | 48 | 53 | 44 |
| B | 17 | 28 | 43 | 29 |
| F: sowing time | | *** | | |
| boron | | *** | | |
| sowing time × boron | | * | | |

* $P<0.005$, *** $P<0.001$

Fig. 1. A symptom of boron deficiency; open flower in two-rowed barley. Left, immediately after ear formation; right, after 3 weeks.

Fig. 2. Ergot in barley partly sterile because of boron deficiency; ergot is abundant in the adventitious shoots.

Fig. 3. Pale coloured barley; open flower because of boron deficiency.

Fig. 4. Symptoms of boron toxicity in barley.

Fig. 5. Boron deficiency (right) in barley and the effect of boron fertilization (left).

Table 8. The effect of boron fertilization on the grain and ergot sclerotia yield of barley and on sterility in five field experiments in 1965—70.

| Year | Grain yield kg/ha | | Yield of ergot sclerotia kg/ha | | Sterile spikelets % | |
|---|---|---|---|---|---|---|
| | 0 | B | 0 | B | 0 | B |
| 1965 | 1 640 | 1 970** | 59.0 | 7.2** | 56 | 12*** |
| 1968 | 2 800 | 3 100** | 61.6 | 0.0*** | 42 | 11*** |
| 1970 | 1 230 | 2 830*** | 42.5 | 0.3*** | 44 | 16*** |
| 1970 | 1 470 | 3 200*** | 63.0 | 2.0*** | 59 | 14*** |
| 1970 | 1 790 | 3 670*** | 40.0 | 1.2*** | 41 | 12*** |
| Mean | 1 790 | 2 950*** | 53.2 | 2.3*** | 49 | 14*** |

B = boron fertilization, 565—1 400 g/ha B
0 — B: ** P<0.01, *** P<0.001

time from 49 % to 14 %. The grain harvest rose in pace with the fertility of barley. The ergot sclerotia yield was abundant when there was an abundance of sterility. The barley cultivars were six-rowed ones.

In the four experiments of 1969 and 1970 (Table 9) without boron fertilization there were ergot sclerotia in some 10 % of the sterile spikelets. The total amount includes spikelets which normally remain sterile. Such sterile spikelets are not infected by the ergot fungus, presumably because of incomplete pistil development. This "basic sterility" was about 10 % in six-rowed barley, and about 3 % in two-rowed. Thus, there were ergot sclerotia in 13 % of the sterile spikelets where there was a sound ovary capable of functioning. The ergot decreased as the fertility increased. The boron fertilization reduced the number of sterile spikelets in which there was functioning ovary in 84 % of the six-rowed and in 93 % of the two-rowed barley. This change drastically reduced the potential of the ergot fungus to infect. Boron fertilization eliminated the ergot almost completely.

The symptoms of boron deficiency in bar-

Table 9. The effect of boron fertilization (B) on ergot and sterility of barley in six and two-rowed cultivars in 1969—79. Means of five results are given representing sterility orders of the experiments.

| Sterility order | Percentage of | | | |
|---|---|---|---|---|
| | Sterile spikelets | | Ergot sclerotia | |
| | 0 | B | 0 | B |
| | Six-rowed cultivars | | | |
| 1 | 67 | 29 | 7.3 | 1.24 |
| 2 | 43 | 19 | 4.7 | 0.22 |
| 3 | 30 | 16 | 1.7 | 0.10 |
| Mean | 47 | 21*** | 4.6 | 0.52*** |
| | Two-rowed cultivars | | | |
| 1 | 43 | 5 | 5.4 | 0.14 |
| 2 | 20 | 5 | 2.3 | 0.02 |
| Mean | 32 | 5*** | 3.9 | 0.08*** |

0 — B (six rowed), 0 — B (two-rowed): *** P<0.001

Table 10. The effect of boron fertilization on the content of water-soluble boron in the soil in some one-year experiments. Boron was applied in connection with cultivation of soil.

| Boron g/ha | Years | Number of experiments | HWB in the soil mg/l |
|---|---|---|---|
| 0 | 1969—70 | 6 | 0.14 |
| 1 100 | | | 0.43*** |
| 0 | 1970—77 | 13 | 0.33[a] |
| 250 | | | 0.38[a] |
| 1 000 | | | 0.55[b] |
| 3 000 | | | 1.00[c] |

*** P<0.001
[a–c] as in Table 3

ley included both the empty ears and the ergot, and also the black mould (*Cladosporium herbarum*), which infected the honeydew of the ergot fungus. Honeydew is also a good substrate for other microbes. In one of the deficiency areas in 1967 fungal sclerotia covered by red conidium powder and resembling red "cap-rows" appeared on the cut surfaces of the barley stubble. The fungi were *Fusarium arthrosporioides* and *Fusarium avenaceum*. It is probable that the honeydew of the ergot fungus that already appeared abundantly in the barley in the summer was the substrate for these fungi all the way from the ear down to the base. They were not clearly perceptible until the straw was cut.

## The effect of boron fertilization on the boron content of the soil and plant

In the experiments of 1969—70 (Table 10) the boron fertilization 1.1 kg/ha raised the content of HWB in soil deficient in boron from 0.14 mg to 0.43 mg/l. In 1970—77 the experiments were performed in fields where the initial content of HWB was 0.33 mg/l. Boron fertilization of 3 kg/ha raised the HWB content to 1.00 mg/l. In both experiment groups the rise in boron content per 100 g/ha of applied boron was nearly the same, i.e. 0.020—0.026 mg/l.

In four one-year experiments boron fertilization applied in connection with cultivation of the soil raised the content of HWB by 0.013—0.024 mg/l per 100 g/ha of applied boron (Table 11). The corresponding rise in the boron content of the barley sprouts was 0.29—0.84, and 0.46—0.73 mg/kg DM in the leaves at the heading stage. At the sprout stage the largest percentage rise was caused by the smallest boron quantity. At the heading stage it was by the biggest boron quantity. The value of HWB doubled with 2.4 kg/ha of boron, and the boron content of the leaves with 900 g/ha.

In silty soil, where the content of soluble boron was relatively high, a boron dose of 1.4 kg/ha raised the value of HWB from 0.48

Table 11. The effect of boron fertilization on the amount of water-soluble boron in the soil and the boron content in the leaves of barley in four experiments in 1971. Boron was applied in connection with cultivation of the soil.

| Boron g/ha | HWB in the soil mg/l | Boron mg/kg d.m. | |
|---|---|---|---|
| | | Sprouts | Leaves[1] |
| 0 | 0.36[a] | 3.19[a] | 4.06[a] |
| 150 | 0.38[a] | 4.45[a] | 4.92[a] |
| 600 | 0.44[a] | 5.79[a] | 6.80[a] |
| 2 400 | 0.75[b] | 10.26[b] | 15.33[b] |
| 4 800 | 1.49[c] | 16.95[c] | 39.20[c] |

[1] at the heading stage
[a–c] as in Table 3

Table 12. The effect of different amounts of fertilizer boron on the boron content in the leaves (heading stage) of barley and on the amount of water-soluble boron in the soil in two silty soil experiments. Boron fertilization in connection with cultivation of the soil in 1977.

| Boron g/ha | Boron mg/kg DM in the leaves | | HWB mg/l in the soil | |
|---|---|---|---|---|
| | 1977 | 1978[1] | 1977 | 1980[1] |
| 0 | 11.41 | 7.51 | 0.48 | 0.50 |
| 1 400 | 23.87 | 11.22 | 0.72 | 0.67 |
| 2 200 | 33.44 | 21.18 | 0.81 | 0.67 |
| LSD (t 0.05) | 10.01 | 3.54 | 0.12 | 0.13 |

[1] after-effect

Table 13. The effect of boron fertilization on the boron content in some plants. The results are means of three experiments. The boron was applied to the soil as solubor before sowing.

| Boron g/ha | Boron mg/kg DM[1] | | Difference mg/kg DM Cereals-others |
|---|---|---|---|
| | Barley Oat Wheat | Lettuce Pea Potato | |
| 0 | 3.78[a] | 17.02[a] | 13.24*** |
| 300 | 4.26[a] | 23.18[b] | 18.92*** |
| 1 200 | 6.57[b] | 27.70[c] | 21.13*** |
| 4 800 | 10.56[c] | 41.89[d] | 31.33*** |

[1] The leaves from cereals and lettuce, the shoots from pea and potato; samples taken in July
*** $P<0.001$, [a–d] as in Table 3

to 0.72 mg/l, and a dose of 2.2 kg/ha to 0.81 mg/l. This means 0.015—0.017 mg/l per 100 g/ha of applied boron (Table 12). Three years later the rise in the soluble boron content in the soil was still visible. A boron dose of 2.2 kg/ha tripled the boron content of the leaves compared with the unfertilized plants, both in the fertilization year and in the following year. The rise in the fertilization year was about 0.9 mg/kg DM per 100 g/ha of applied boron.

The boron contents in various plants were compared with one another in three experiments (Table 13). The contents in the leaves of the cereals were at the same level, generally well below 10 mg/kg DM. The boron contents in the shoots of lettuce, pea and potato were generally well above 20 mg/kg DM. The contents in the leaves of the cereals were thus on average only a fifth of the contents of the dicotyledones. In the cereals the rise of the boron content due to boron fertilization was about 0.2 mg/kg DM and in the dicotyledones on average 1.2 mg/kg DM per 100 g/ha of applied boron.

In the fertilization experiment in 1979—80 the boron was applied in the form of granulated NPKB fertilizer by the usual Finnish placement method. 600 g/ha boron tripled the boron content in the leaves and 1.2 kg/ha quintupled it (Table 14). The rise in the boron content of the barley leaves at the early ear stage was 2.27 mg/kg DM per 100 g/ha of applied boron. The effect of renewed boron fertilization on the boron content of the barley leaves was the same as in the previous year. A small difference was observed in content between the flag leaves and the third leaves. More boron had accumulated in the flag leaves than in the third leaves from fertilizers containing limited boron. Less boron had accumulated in the flag leaves than in the third leaves from fertilizers rich in boron. Symptoms of boron toxicity (brown necrotic spots) were most abundant in the lowest leaves. There were very few in the flag

Table 14. Results of boron fertilization applied in compound NPKB fertilizer by placement. The effect on the boron content in barley and soil in sandy soil. Same fertilization in 1979 and 1980.

| NPKB fertilizer | | Boron mg/kg DM in the leaves at the heading stage | | | | B-[1] toxicity 0—100 1980 | HWB in soil mg/l 1980 |
|---|---|---|---|---|---|---|---|
| kg/ha | B-% | 1979 | 1980 | | 1981 | | |
| | | | flag leaf | third leaf | | | |
| 315 | 0.00 | 6.8[a] | 7.2[a] | 5.5[a] | 7.0[a] | 0 | 0.51[a] |
| 315 | 0.05 | 10.5[b] | 10.9[a] | 6.7[a] | 7.0[a] | 0 | 0.51[a] |
| 315 | 0.1 | 14.5[c] | 12.5[b] | 9.2[b] | 6.5[a] | 1 | 0.59[a] |
| 315 | 0.2 | 18.5[d] | 20.7[c] | 22.5[c] | 8.5[a] | 5 | 0.70[b] |
| 315 | 0.4 | 30.9[e] | 20.6[c] | 25.3[c] | 9.9[a] | 17 | 0.87[b] |
| 630 | 0.00 | 7.1[a] | 8.0[a] | 5.6[a] | 7.1[a] | 0 | 0.54[a] |
| 630 | 0.05 | 12.7[b] | 17.3[b] | 9.7[b] | 6.0[a] | 1 | 0.65[a] |
| 630 | 0.1 | 21.5[c] | 33.4[b] | 23.3[c] | 8.5 | 8 | 0.87[b] |
| 630 | 0.2 | 33.2[c] | 47.2[c] | 50.5[d] | 9.0[b] | 17 | 1.03[b] |
| 630 | 0.4 | 71.4[d] | 49.9[c] | 63.6[d] | 12.9[b] | 47 | 1.27[c] |
| 945 | 0.00 | 8.1[a] | 11.2[a] | 7.1[a] | 5.9[a] | 0 | 0.58[a] |
| 945 | 0.05 | 17.0[b] | 19.8[b] | 14.9[b] | 6.2[a] | 1 | 0.73[a] |
| 945 | 0.1 | 29.9[c] | 50.6[c] | 45.9[c] | 7.7[b] | 22 | 1.08[b] |
| 945 | 0.2 | 57.1[d] | 67.4[d] | 95.0[d] | 11.4[c] | 48 | 1.24[b] |
| 945 | 0.4 | 93.3[d] | 78.7[d] | 126.0[d] | 13.8[d] | 70 | 1.65[c] |

[a—d] same as in Table 3

[1] Visual estimation of the number of necrotic blotches in the leaves (0 = no blotches)

Table 15. The fertilization method experiment with barley in 1979—80. Broadcast fertilization in connection with cultivation, row-fertilization by placement.

| NPKB fertilizer | | Fertilization method | Boron in the leaves mg/kg DM | | Symptoms of boron toxicity 0—100[1] 1980 | HWB in soil mg/l | |
|---|---|---|---|---|---|---|---|
| kg/ha/μ | B-% | | 1979 | 1980 | | 1980 | 1982 |
| 500 | 0.0 | broadcast | 7.7[a] | 7.2[a] | 0 | 0.48[a] | 0.51[a] |
| 500 | 0.0 | row | 7.9[a] | 7.2[a] | 0 | 0.46[a] | 0.53[a] |
| 500 | 0.2 | broadcast | 21.6[b] | 21.0[b] | 7 | 0.90[b] | 0.49[a] |
| 500 | 0.2 | row | 23.6[b] | 39.5[c] | 31 | 0.83[b] | 0.58[a] |
| 800 | 0.0 | broadcast | 6.1[a] | 7.5[a] | 0 | 0.51[a] | 0.46[a] |
| 800 | 0.0 | row | 7.5[a] | 9.9[a] | 0 | 0.55[a] | 0.49[a] |
| 800 | 0.2 | broadcast | 22.5[b] | 43.3[c] | 18 | 1.29[b] | 0.52[a] |
| 800 | 0.2 | row | 34.8[c] | 75.3[d] | 56 | 0.97[b] | 0.55[a] |

[a—d] (NPKB 500), [a—d] (NPKB 800) same as in Table 3
[1] same as in Table 14

leaves and none at all in the straw. One year after the last boron fertilization the differences between the boron contents in the leaves were small. In the autumn of the latter fertilization year 30 to 40 % of the boron applied during the two years was detectable in the soil as water-soluble B. Three years after the beginning of the experiment no differences in the content of soluble boron in the soil were observed.

In the fertilization method experiment (Table 15) boron was applied in NPKB granules by the placement method and broadcast method during the two succeeding years. Placement of as little as 1 kg/ha of boron per year caused distinct toxic symptoms in the leaves of barley during the latter experimental year. The same amount of boron applied as broadcast fertilization scarcely caused any visible damage to the barley. The boron content in the leaves increased during the first year by 1.16 with broadcast fertilization and by 1.65 mg/kg DM with placement fertilization of 100 g/ha of boron. The water-soluble boron in the soil increased thanks to the boron fertilization in two years by about 0.02 mg/l per 100 g/ha of applied boron. After three growth periods from the last fertilization there were no differences in the contents of water-soluble boron in the soil.

The boron content in barley straw and grain was not determined for all the experiments. The boron content of these plant parts from B-deficient soils not given boron fertilization was 2—3 mg/kg DM. Boron fertilization raised the content of boron by about 0.05—0.18 mg/kg DM per 100 g/ha of applied boron.

The total boron was determined from a $Na_2CO_3$-melt for some soil samples in the boron experiments. The boron amounts differed very little. In the 18 samples examined the boron averaged 32.9 mg/kg, varying between 27.2 and 38.0 mg/kg. The content of water-soluble boron in the same samples averaged 0.50 mg/l. The volume weight of the soil samples was 1.0, so the numerical values can be directly compared. Thus, about 1.5 % of the total boron in the soil was water-soluble. Some of the samples were from plots where boron fertilization had not been applied. Some had received amounts of boron for two years. There were 11 comparative pairs of this kind in this material. The total amounts of boron in the unfertilized plots averaged 31.3 mg/kg and 33.5 mg/kg in those which had received boron. The amounts of

water-soluble boron from the same samples were 0.40 and 0.53 mg/l. The differences were statistically significant. Of the boron applied (on average 2.49 mg/l) some 88 % was seen as an addition to the total boron, and about 5 % as an addition to the soluble boron in the soil.

## DISCUSSION

### Sterility

Numerous field experiments performed over a long period, provide conclusive evidence that the widespread open-flower-ergot-sterility syndrome in barley was caused by boron deficiency, and could therefore be repelled with boron fertilization. In experiments where boron fertilization reduced sterility in barley by at least half of the original, the sterility averaged 42 % (unfertilized with boron) and 14 % (fertilized with boron). Generally 300—600 g/ha of boron sufficed to correct the deficiency. The boron fertilizer could be applied in connection with cultivation of the soil or as foliar spray. A good fertilization result was achieved with as little as 150 grams of boron per hectare. Since 1973 Finnish NPK fertilizers have contained 0.03 % B. After compound fertilizers containing boron became common in Finland, deficiency symptoms in barley cultivation disappeared. This demonstrates the cause and effect relationship between sterility and boron deficiency. A 0.03 % boron content in the compound fertilizers has proved sufficient for barley.

In "empty ear" areas of barley cultivation, the contribution of liming to the outbreak of symptoms could be stated. Lime had been added for many years, perhaps ten years earlier. Healthy barley started to grow when the liming stopped. The most sterility occurred where lime loads had been dumped for further spreading. In those sites the pH of the soil was high (pH 7) and Ca over 5 000 mg/l. Sterility analyses of barley from three such areas showed that 81—96 % of the spikelets were empty or exhibited ergot sclerotia. In the adjacent barley, 20—40 % were empty spikelets. The contribution of liming to the crop failure was obvious. The cause and effect relationship between liming and pH and boron deficiency was mentioned by DECAU (1960), GUPTA (1972) and also by PRASAD and BYRNE (1975). ØDELIEN (1937) has stated that the damage caused by excessive liming of Norwegian peat soils can be corrected with boron fertilization. According to PHILIPSON (1953), a rise in pH owing to liming improves the solubility of the boron, but later binding of the boron in an insoluble form caused by Ca remains permanent. In experiments by ERVIÖ (1981) and SAARELA (1985), liming reduced the uptake of boron by the barley. In the one-year liming experiments of the present study the liming did not increase the sterility of barley, and in some cases it may even have reduced it slightly.

The amount of hot water soluble boron in the soils of the deficiency areas was generally 0.05—0.2 mg/l. At those contents sterility appeared and boron fertilization generally reduced it. In experiments where boron substantially reduced the sterility of barley and in plants for which the boron content was determined, the boron content of the leaves of barley not fertilized with boron 3.74 averaged at the sprout stage, and 2.89 mg/kg DM at the heading stage. The amounts mentioned do not justify any conclusions concerning boron deficiency symptoms on the basis of contents of boron. The appearance of boron deficiency in harvested barley could not be predicted from the boron content of the sprouts.

In the barley of the deficiency areas there was generally substantial variation in the level of sterility. The barley was more sterile in limed parts of the field and where the lime loads were dumped, as was also the case in small areas of coarse soil and on strips near open ditches. Areas near old open ditches in some underdrained fields appeared to be healthier. Moisture conditions were obviously better in these areas than in other parts of the field, even during a dry summer. Nutritious top soil had also accumulated in these areas. Barley at the flower building stage could take up sufficient boron.

In areas of shrivelled-head barley, differences between various cultivars and shoots of barley were noted in the sterility of the ears and the spikelets. Sterility differences also appeared between populations of the same cultivars sown on different dates. In the experiments the effect of the sowing time of the cultivars was not regular. The results, however, justify the conclusion that differences in the growth rhythm of the barley cultivars may lead to differences in sterility. Generally the adventitious shoots were the most sterile. The varying degrees of sterility in ears in the present research can be attributed to varying degrees of boron deficiency. The sensitivity of the adventitious shoots to boron deficiency is mentioned e.q. by KORONOVSKI (1961). Research by AHOKAS (1979) on cytoplasmic male sterility shows that the latest tillers tended to be most male sterile in the partially restored barley.

A fertile barley flower may open slightly at pollination time because of swelling in the lodicules, the flower parts at the base of the ovary. When no pollination occurs the flower opens again. This opening is caused by the swelling of the ovary. The flower remains open for 7—8 days. When the ovary dries and collapses, the flower closes (HACKET and ESLICK 1968).

Pollen sterility of barley caused by boron deficiency also leads to this open-flower phenomenon. The symptoms and the course of events are the same as those described above. Incomplete stamens could be found in the barley in the boron deficiency areas and in the boronless plots of the experiments. The ovary swelled and the flowers opened slightly if the ovule remained unfertilized. Many earlier studies have shown that the development of the stamen, pollen germination and pollen tube growth require boron (SCHMUCKER 1935, KORONOVSKI 1961). DROZDOV and KUTUZOV (1960) have indicated that the most critical stage from the point of view of the supply of boron for the barley flower is the formation time of the first anther loculi. Boron deficiency also causes restricted root growth (BUSSLER 1960). The effect of the disturbances in root development becomes more pronounced in dry conditions. This concerns also pollen sterility caused by boron deficiency.

It was stated in the preliminary experiments that the early flattened corn of barley caused sterility. It can be concluded, that the horizontal position of the ear at the flowering stage makes the access of the pollen grain on the stigma difficult. The pollination becomes incomplete, although the pollen is faultless. Laid barley corn may be a consequence of both rain, and also of a sudden collapse of the turgor caused by dryness. Dryness and laid corn can then make the supply of boron more difficult. As a consequence of the early laid corn, swelling of the ovary and open flower similar to that in the boron deficiency of barley was noted.

Only guesses can be made about what it is that forces the ovary to swell in cases where no fertilization occurs. Such a reaction is in fact rational; there is "reason" for the functions of the flower. They secure fertilization. When the flower is open, the access for the functioning pollen is free. The experimental results do not reveal how large a percentage of the ovules of the open-flowers were fertilized by the foreign pollen. Such fertilizations naturally occurred mostly where there was functioning pollen at the right time in the same ear or in a nearby

ear, and where the conditions for the spreading of the pollen were favourable.

It is probable that the boron deficiency in barley did not appear earlier, not at least in any larger areas. Which change in cultivation method caused the symptoms in the 1960s? Three important changes can be seen: increased liming, increased use of main nutrients, and reduced rotation of the nutrients. Effective open cultivation and increased leaching of boron may lead to boron deficiency, especially in soils poor in boron.

A sufficient supply of many trace elements was once secured by their presence as impurities in the fertilizers. Abundant use of "cleaner" fertilizers brought about a scarcity of trace elements in the soil. This does not quite hold true regarding boron, as it was hardly an impurity in fertilizers. On the other hand, it could be assumed that changes in the fertilization method have affected the boron uptake by plants. In the 1960s, larger scale application of granulated compound fertilizers began; placement was also used. As a consequence, the boron supply of the barley obviously decreased in proportion to the main nutrients.

## Ergot

Ergot was the first symptom of boron deficiency noted (TAINIO 1961). The ergot fungus (*Claviceps purpurea* (Fr) TUL) was first revealed by the honeydew. Later on, the sclerotia became visible. Some of them were many centimeters long. They had the tendency to come off the spikelet before harvesting, fall to the ground and thereby perpetuate the ergot contamination. Some entered the seed crop and returned through harvesting to the field with the seed. If the barley received boron fertilization, there was very little ergot or none at all. Most ergot was found in the adventitious shoots.

The abundance of the ergot in barley was obviously affected by factors which also affected pollen sterility in the barley. The ergot fungus infection presupposed that the barley flower was open for a sufficiently long time and that the ovary was functional. The spikelets of the barley in the severe boron deficiency areas were open a long time. Many weeks elapsed between the appearance of the open spikelets of the main shoots and the drying of the last ovaries of the adventitious shoots. Throughout this time the spores and conidiums of the ergot fungus were in the position to infect part of the barley. The flower was perhaps fertilized after many days of waiting by a foreign pollen which was conveyed by air currents. They were susceptible to ergot contamination throughout this whole time. The results suggest that the construction of the spikelets may affect infection of various barley cultivars by the ergot fungus.

The attack of the ergot fungus depends on both the predisposition of the barley and also on how many fungus spores and conidiums are on the move at just the right time. The best sources of contamination are grasses on ditch banks. There are even more spores than normal, if the preceding crop has been rye or seed hay contaminated by ergot. They are cross-fertilizing and have open flowers. Ergot is often abundant in them. Infection by the ergot fungus is also influenced by many factors, e.g. the weather, which promote or hamper germination of the ergot sclerotium as well as the spreading of the spores and conidiums.

The ergot in many other studies has been found to be a bad parasite in male-sterile grain (HAYES 1968, RAPILLY 1969). In RAPILLY's experiments, the sclerotium developed in all male-sterile wheat flowers which had been contaminated before pollination. DARLINGTON and MATHRE (1976) stated that the resistance of the wheat to the infection of the ergot fungus developed on some ms-lines with in a couple of hours of pollination, and on most in 7 days.

Ergot was cultivated in Finland in the 1960s and in the early 1970s because of the medicine it contained. Fungus contamination was

achieved by inoculating ears of rye prior to the flowering with the conidium suspension of the ergot fungus conidium grade, *Sphacelia segetum* Lev. (RUOKOLA 1956). Refined ergot strain was used for the inoculation. The ergotamine concentration was tens of times stronger than that in the native Finnish ergot. When applying the results of the present research it may be possible to avoid a violent contamination method. The inoculation could be carried out by spraying conidiums and spores into the open flowers of barley. Amounts of ergot sclerotia corresponding to a harvest of 400 kg/ha were received from the observational plots. Cultivation of ergot would also be the best possible application of biotechnics. The difficulty is to obtain a sufficient amount of male-sterile barley. On the other hand, cultivations of ergot rich in alkaloides in the fields constitute an environmental risk. There will hardly be a return to this cultivation method as ergotamine is nowadays made synthetically.

### The boron content in plant and soil

In the arable fields of Finland in 1966—70, hot water extractable boron averaged 0.39 mg/l, and 0.64 mg/l (KÄHÄRI et al. 1987) in 1981—85. The rise may be due to the small amount of boron added to the compound fertilizers. In a large global study by SILLANPÄÄ (1982) the content of water-soluble boron in 90 Finnish wheat fields was 0.55 mg/l. In the areas of boron deficiency where the field experiments of the present study were situated, there was 0.05—0.20 mg/l of hot water soluble boron in the soil. At this content boron fertilization often had a definitely positive influence on the barley grain harvest. Toxicity symptoms of boron — brown necrotic spots in the leaves (BERGMAN 1985) — were found in barley when the content of soluble boron in the soil exceeded 0.8 mg/l. The desired content of soluble boron in the soil may be 0.3—0.7 mg/l on the basis of these results. A sufficient content of soluble boron in acid soil was 0.45—0.65 mg/l in SAARELAS pot experiments (1985). This content sufficed for a full seed harvest of turnip rape. GUPTA (1972) stated that the toxic effect of boron reduced barley crops when there was more than 0.5 ppm of boron in the substrate. The margin between necessary and excessive boron is small.

The experimental material does not provide any definite knowledge about the loss of soluble boron from the soil after boron fertilization. The results suggest that differences in the soluble boron contents between a soil fertilized or not fertilized with boron disappear in a relatively short time. According to TÄHTINEN (1970), the effect of boron fertilization on the soluble boron content in the soil decreases quickly, but may still be visible after 4—6 years.

In soil with little boron, the boron content in the leaves of barley at the ear formation stage was 2—6 mg/kg DM. This amount was generally smaller than the boron content at the sprout stage. Boron fertilization applied in connection with cultivation of the soil or as foliar spray increased the boron content in the leaves by about 0.6 mg/kg DM per 100 g/ha of applied boron. Boron applied by placing in compound fertilizer granules increased the boron content by 1.6—2.2 mg/kg DM per 100 g/ha of applied boron. Symptoms of boron toxicity were found in barley in which the boron content in the leaves was over 25 mg/kg DM. On the basis of these results the desired boron content in the leaves at the ear formation stage, can be considered 6—20 mg/kg DM. GUPTA (1972) has stated that boron deficiency reduces crops when the boron content in the barley tissue at the boot stage remains under 2 ppm, and that the toxic effect of boron reduces crops if the boron content is over 14 ppm. The results of the present experiments do not contradict GUPTA's conclusions.

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*Manuscript received September 1990*



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## SELOSTUS

# Ohran boorinpuutos


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Eri puolilla Suomea esiintyi ohrassa 1960-luvun puolivälistä alkaen runsaasti avokukkaisuutta, kahutähkäisyyttä ja torajyväisyyttä. Tätä oireyhtymää ja sen syitä tutkittiin pääasiassa vuosien 1965—72 aikana, tiettyjä yksityiskohtia myöhemminkin, järjestämällä kenttäkokeita yksityisille maatiloille. Useimmat kokeet olivat Keski-Suomessa.

Ohran avokukkaisuus — torajyväisyysoireisto osoitettiin boorinpuutteen seuraukseksi. Kukan avasi paisuva sikiäin.

Sikiäimen paisuminen taas johtui boorin puutteen aiheuttamasta siitepölysteriiliydestä. Pahimmilla katoalueilla jopa 80 % ohran kukista oli steriilejä. Kalkituksella ei yksivuotisissa kokeissa ollut vaikutusta boorinpuutokseen. Fertiliys palautui ja jyväsato kohosi normaalitasolle 350—600 g/ha booriannoksella, joka annettiin muokkauksen yhteydessä tai ruiskutteena oraille. Steriiliys väheni selvästi jo 160—300 g:lla/ha booria. Koealueilla, joilla boorilannoituksella oli selvä vaikutus ohran steriiliyteen, oli maassa helppoliukoista booria 0.05—0.2 mg/l ja orasasteen lehdissä booria n. 3 mg/kg/ka. Oraan booripitoisuudesta ei voitu ennustaa puutoksen ilmenemistä steriiliytenä. Jälkiversot olivat steriilimpiä kuin pääversot. Boorilannoitus vaikutti samalla tavalla monitahoisten ja kaksitahoisten lajikkeiden steriiliyteen.

Ohran boorinpuutteeseen liittyi torajyvien esiintyminen. Torajyväsienen (*Claviceps purpurea* (Fr.) TUL.) iskeytymisen teki mahdolliseksi kukkalehtien avautuminen, jonka aiheutti sikiäimen paisuminen siitepölysteriilissä ohran kukassa. Yleensä torajyviä oli runsaasti, jos siitepölysteriiliytä oli runsaasti. Tästä syystä jälkiversoissa oli usein eniten torajyviä. Tähän vaikutti myös sekundäärisen torajyväsaastunnan runsaus jälkiversojen kukkien avautuessa. Tutkimuksen tulosten perusteella ohran siitepölysteriiliyden hyväksikäyttöä torajyvän viljelyssä voidaan pitää mahdollisena.

Boorilannoitus lisäsi kuumaan veteen liukenevan boorin pitoisuutta maassa 0.02 mg/l annettua 100 g/ha boorierää kohden. Boorimyrkytysoireita ohrassa todettiin, jos maan helppoliukoisen boorin pitoisuus oli yli 0.8 mg/l. Ohran lehtien booripitoisuus tähkälletulovaiheessa nousi keskimäärin 0.6 mg/kg/ka hajalannoituksena annettua 100 g/ha boorierää kohden. NPK-seoslannoitteen rakeessa sijoittaen annettu boori nosti lehden booripitoisuutta vastaavasti 2 mg/kg/ka. Viljojen lehdissä booria oli n. 1/5 kokeessa olleiden kaksisirkkaisten eli herneen, perunan ja salaatin versojen booripitoisuuksista. Maan kokonaisboorista (n. 33 mg/kg) oli helppoliukoista 1.5 %. Tavoiteltava maan helppoliukoisen boorin pitoisuus ohran viljelyssä lienee 0.3—0.7 mg/l ja tavoiteltava ohran lehtien booripitoisuus tähkälletulovaiheessa 6—20 mg/ka/ka.

ANNALES AGRICULTURAE FENNIAE, VOL. 30: 407—413 (1991)

Seria AGROGEOLOGIA ET -CHIMICA N. 166 — Sarja MAA JA LANNOITUS n:o 166

# CADMIUM AND SULPHUR CONTENTS OF DIFFERENT PLANT SPECIES GROWN SIDE BY SIDE

MIKKO SILLANPÄÄ and HÅKAN JANSSON

SILLANPÄÄ, M. and JANSSON, H. 1991. **Cadmium and sulphur contents of different plant species grown side by side.** Ann. Agric. Fenn. 30: 407—413. (Agric. Res. Centre of Finland, Inst. Crop and Soil Sci., SF-31600 Jokioinen, Finland.)

The cadmium and sulphur contents in the dry matter of different parts of 16 crops grown side by side at nine locations in various parts of Finland were determined and compared.

The highest average cadmium content of various plants or plant parts exceeded hundredfold the lowest content. When comparing different parts of the same plant the greatest, a 19-fold difference, was found between pea seed and its stalk. In other crops 3—4 -fold differences were common.

In general, cereal grains were low in Cd. The Cd contents of hay crops were equal or slightly higher than Cd in grains but lower than in straws of the cereal crops. The most effective Cd collectors were root crops, that had generally higher mean Cd contents both in their tops and roots than the other crops under comparison.

The sulphur contents of different crops varied less than those of Cd, i.e. the difference between the lowest and highest mean S content was only 18-fold. Also the differences between different parts of the same plant were smaller.

Swede and turnip rape were the richest but also turnip roots, pea stalks and onions were high in S. The lowest S contents were found in sugar beet and carrot roots. Also both the grain and straw of cereal crops, as well as timothy dry hay, were relatively low in S. Rye grass contained more S than the other hay crops studied.

Index words: cadmium content, sulphur content, cereals, timothy, red clover, rape, ryegrass, pea, onion, turnip, carrot, beet, swede.

## INTRODUCTION

Although cadmium may be beneficial to animals in very small quantities (e.g. ANKE et al. 1986) it is generally considered a non-essential element for both plants and animals. Its importance lies in its toxicity and, therefore, the Cd contents of plants are of the greatest concern as both a Cd reservoir and a pathway of Cd to man and animals. Thus, the differences between plant species in their absorption rate of Cd are important from the environmental and health standpoints.

Although non-essential to plants, Cd is effectively absorbed by both the root and leaf systems. Soil factors such as pH may affect its availability to plants (e.g. CHANEY and HORNICK 1977) and a part of the Cd found in plants is airborne, falling as either wet or dry depositions.

Sulphur is an essential nutrient for both plants and animals. It plays an important role in protein synthesis and is a constituent of some enzymes and vitamins such as $B_1$- and the H-vitamins. Its metabolic functions are quite well-known.

Sulphate is the form in which plants absorb S from the soil. In addition to native S, soils receive S from the atmosphere or in fertilizers containing S along with the major nutrient being applied, e.g. ammonium or potassium sulphate. The quantities of airborne S depend on proximity to the sea, rainfall and on the emission of $SO_2$ in smoke. There is also evidence that plants can directly utilize atmospheric $SO_2$ as a part of their S supply (e.g. FALLER et al. 1970). Although the contents of S in plants are of the same order as those of P, the application of S does not generally play as important role as P fertilization. The trial fields of this study received 8.8 kg S/ha in the NPK fertilizers. The atmospheric fall-out of S in Finland has been estimated to be about 15 kg/ha/yr in the southern parts of the country but considerably less in the north (e.g. TUOVINEN et al. 1990).

Despite the availability of data on the Cd and S contents of different plant species and parts (e.g. BERGMANN 1983, BERGMANN and NEUBERT 1976), they are seldom strictly comparable because they often originate from plants grown on dissimilar soils. Another factor causing heterogeneity in the data on plant Cd content is variation in the analytical methods employed by different scientists and also the variable role of airborne Cd and S from one location to another.

In an attempt to eliminate the above distruptive factors and improve the comparability between various plant species, the crops in this study were grown side by side and analysed in one laboratory by the same methodology.

## MATERIAL AND METHODS

The locations of trial sites, collection of samples and their preliminary treatment have been described in an earlier paper (YLÄRANTA and SILLANPÄÄ 1984). General soil properties and extractable Cd and S contents of the experimental soils are given in Table 1.

Soil Cd was extracted using an acid ammonium acetate-EDTA solution (0.5 M $CH_3COONH_4$, 0.5 M $CH_3COOH$, 0.02 $Na_2EDTA$, pH 4.65) as the extractant (LAKANEN and ERVIÖ 1971) and S with acid ammonium acetate, pH 4.65 (VUORINEN and MÄKITIE 1955). In both cases the extracting ratio was one to ten by volume and the extracting time was 1 h. Cd concentrations were determined from the solution by flame atomic absorption spectrometry and S with a plasma emission spectrometer.

For determination of Cd and S from plant materials samples of 0.5 g were digested in 5 ml of conc. $HNO_3$ overnight then diluted to 50 ml in volume bottles. S was determined with a plasma emission spectrometer and Cd by electrothermal atomic absorption spectrometry using the Zeeman effect for background correction. The procedure is described in detail by KUMPULAINEN and PAAKKI (1987).

## RESULTS AND DISCUSSION

**Cadmium.** The average AAAc-EDTA extractable Cd content of the soils of the nine trial sites of the present study, 0.07 mg/l (Table 1), was slightly higher than the mean (0.06 mg/l) of the 207 Finnish soils reported by SIPPOLA and MÄKELÄ-KURTTO (1986) but lower than the mean (0.076 mg/l) of a larger material (1320 soils) studied by ERVIÖ et al. (1990). Thus, the Cd contents of different plants reported here are likely to reflect the general Cd levels in Finnish agricultural crops.

The variation between the Cd contents of different plant species was very wide (Fig. 1). The highest contents measured from sugar beet tops exceeded a hundredfold those of the lowest, pea seed. Also within individual plants, the differences in Cd concentrations were considerable. The relatively greatest difference between different parts of the same plant were found in pea (19-fold) but also in cases of wheats, turnip rape, swede and sugar beet 3—4 -fold differences were detected.

In general, cereal grains had low Cd contents, the mean values varying from 0.03 to 0.09 ppm, but their straws contained considerably more Cd, from 0.13 to 0.26 ppm in DM. The above values are in good agreement with those reported by SYVÄLAHTI and KORKMAN (1978) and VARO et al. (1980 b) for cereal grains, 0.02—0.10 and 0.02—0.08 ppm in DM, respectively.

The contents of Cd in hay crops, including red clover were about equal or only slightly higher than those in cereal grains. The Cd averages of various cuts of timothy varying from 0.034 to 0.058 ppm are somewhat higher than those (aver. 0.017 ppm) reported by SIPPOLA and MÄKELÄ-KURTTO (1986) from Finland but lower than the mean Cd contents of grasses in eight countries reported by KABATA-PENDIAS and PENDIAS (1984): West Germany 0.07, Poland 0.08, Iceland 0.10, the U.S. 0.16, France 0.16, Canada 0.21, DDR 0.27 and Czechoslovakia 0.6 ppm in DM.

The most effective Cd collectors were root crops, having generally higher mean Cd contents (0.1—0.7 ppm) both in their tops and roots than the other crops under comparison. The good availability of soil Cd to plants may explain the high Cd contents in the roots of the root crops studied but it cannot explain the still higher Cd concentrations in their tops (see e.g. swede and sugar beet in Fig. 1). For example,

Table 1. General soil properties and acid ammonium acetate-EDTA extractable cadmium and ammonium acetate extractable sulphur contents of topsoils at the experimental sites.

| Site | Soil type | Org. C % | pH ($CaCl_2$) | Electr. cond. $10^{-4}$ S/cm | Cd (extractable) mg/l | S (extractable) mg/l |
|---|---|---|---|---|---|---|
| 1. Häme Res. Sta. | Sandy loam | 1.7 | 5.3 | 0.9 | 0.09 | 29 |
| 2. Sata-Häme Res. Sta. | Silty clay | 3.8 | 5.1 | 2.0 | 0.10 | 33 |
| 3. S.W. Finland Res. Sta. | Sandy clay | 1.7 | 4.0 | 1.6 | 0.05 | 105 |
| 4. S. Savo Res. Sta. | Finesand | 4.4 | 4.8 | 1.5 | 0.06 | 35 |
| 5. Dept. of Soil Science | Heavy clay | 4.7 | 4.5 | 1.8 | 0.08 | 53 |
| 6. Central Finland Res. Sta. | Finesand | 1.5 | 4.8 | 0.9 | 0.05 | 25 |
| 7. Kainuu Res. Sta. | Carex peat | 47 | 4.1 | 1.3 | 0.01 | 39 |
| 8. N. Savo Res. Sta. | Mould soil | 16 | 4.6 | 4.2 | 0.08 | 51 |
| 9. S. Ostrobothnia Res. Sta. | Mould soil | 19 | 4.9 | 2.3 | 0.07 | 84 |
| Mean | | | 4.7 | 1.8 | 0.07 | 50 |
| ±s | | | 0.4 | 1.0 | 0.03 | 27 |

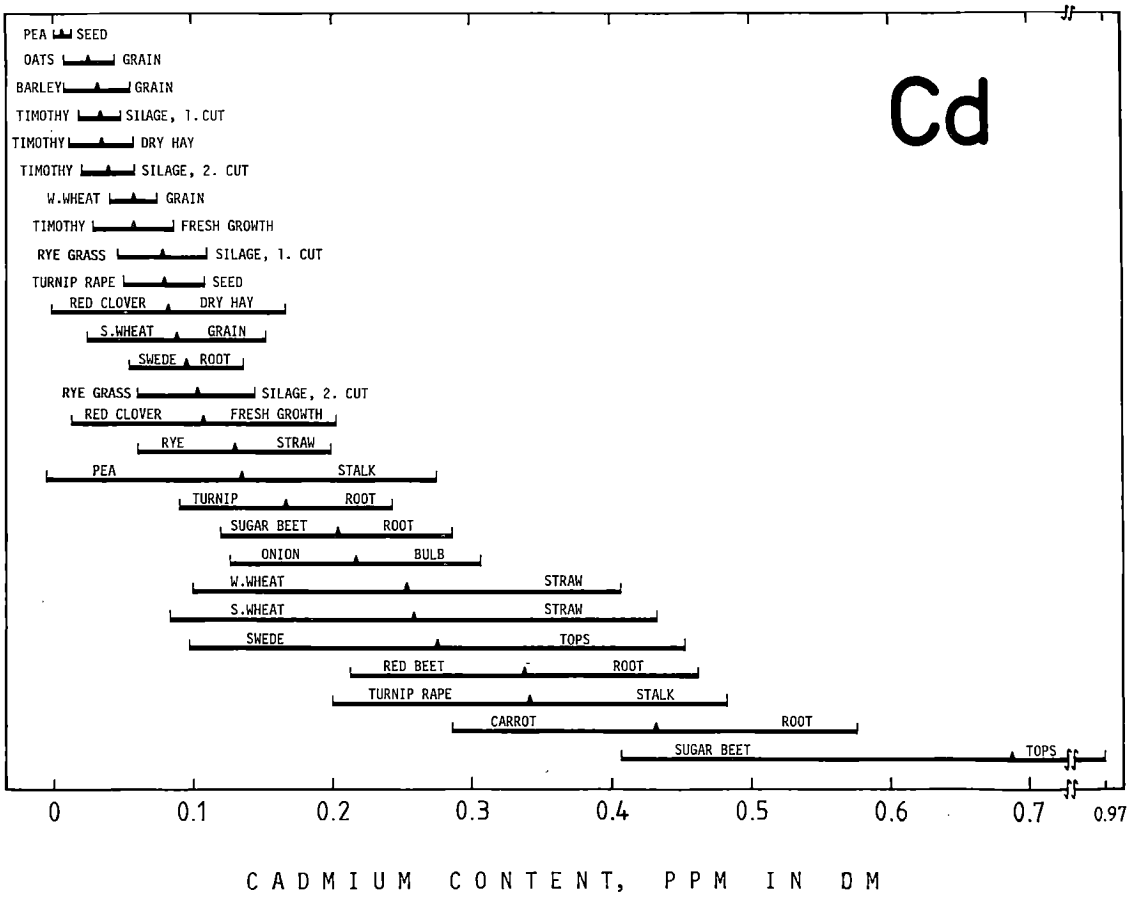


Fig. 1. Two-year averages (x ± s) of cadmium contents of different parts of 16 crops grown side by side.

KABATA-PENDIAS and PENDIAS (1984) reviewed the mechanisms of Cd transportation in plants and concluded that although the roots can take up large amounts of Cd from the growth medium, its translocation throughout the plant may be restricted because Cd is easily retained in the exchange sites of active compounds located in cell walls. A partial explanation for the high Cd contents in the tops of the root crops studied may be that their broad leaves have received much more exposure to external Cd contamination from the air than those of the other crops.

**Sulphur.** The acid ammonium acetate extractable S contents of the experimental soils (Table 1) were higher than those reported from Finnish soils e.g. by ERVIÖ et al. (1990), averaging 19 mg S/l. This is partly due to the relatively high representation in this study of coastal soils, which (e.g. sites 3 and 9) are located in areas where so-called sulphate soils are common. Still, even the highest S contents here were much lower than those of real sulphate soils. For example ERVIÖ and PALKO (1984) present 232 mg S/l as an average for 212 sulphate soils located in the northwestern coastal area of Finland.

The S contents of different plant species varied much less than, for instance those of Cd (Fig. 2). The highest S content, 0.91 % in swede

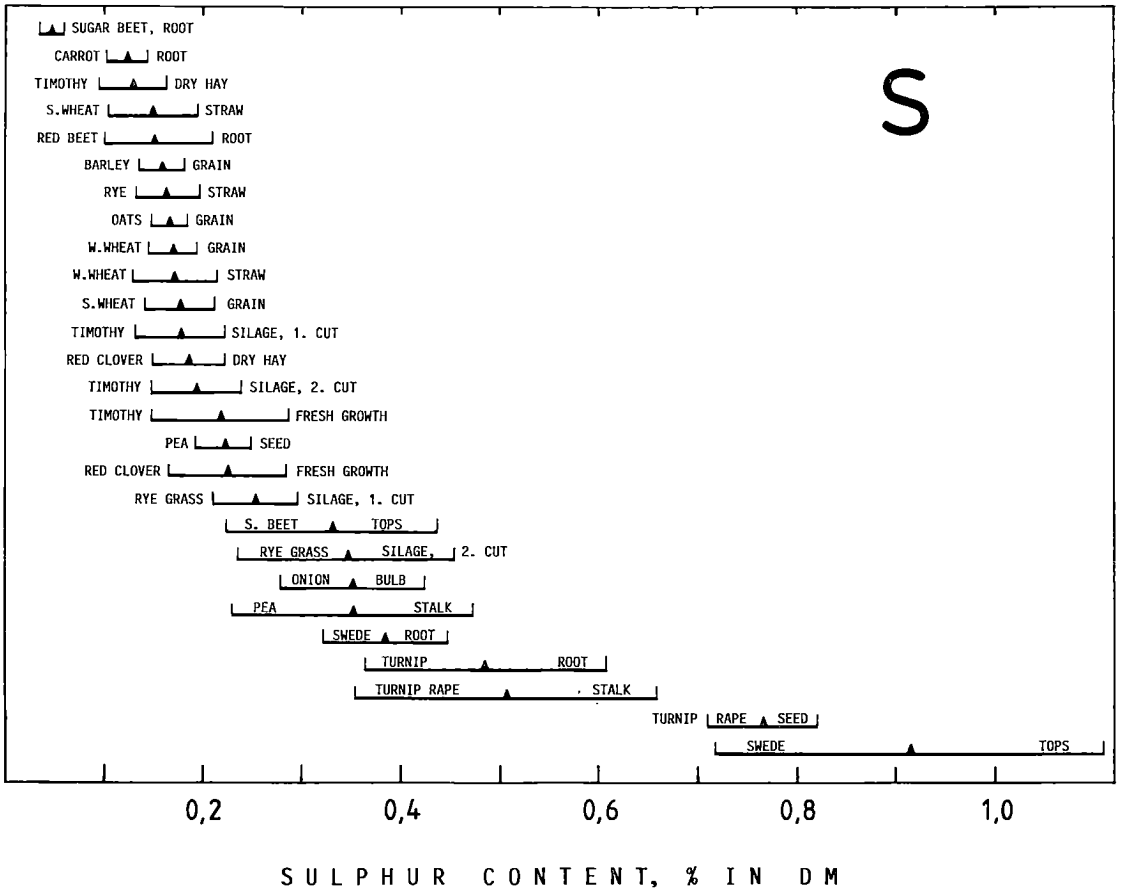


Fig. 2. Two-year averages ($x \pm s$) of sulphur contents of different parts of 16 crops grown side by side.

tops, exceeded the lowest, 0.05 % in sugar beet roots, by a factor of 18 and the next lowest, 0.12 % in carrot roots, by a factor of 7.5.

Within individual plants the variations in S concentrations were relatively narrow. Only the S content of sugar beet tops exceeded that of its roots by a factor of 6.6. In the other crops studied for which comparison was possible, these factors were $<2.0$ and in some cases, e.g. wheat grains vs. straw, the factors approached 1.0.

Of the crops and their parts analysed, the richest in S were swede and turnip rape, in which crops' all parts were high in S. High S concentrations were also measured in turnip roots, pea stalks and onions. In sugar beet, S seems to be concentrated in the tops while its roots contain very little. Also the roots of the other root crops, carrot and red beet, were low in S, 0.1—0.2 % in DM. Cereal crops, both the grain and straw, contained somewhat more S but generally below 0.2 %. Timothy and red clover, when harvested at the dry hay stage, contained less S than if harvested at earlier physiological stages (silage or fresh growth). Rye grass contained somewhat more S than the other hay crops studied.

Of the above crops or parts of crops, ten were the same as those studied by VARO et al. (1980 a, b). They reported very similar mean S

contents: carrot root 0.13, redbeet root 0.16, barley grain 0.16, oat grain 0.17, winter and spring wheat grains 0.16, pea seed 0.20, onion 0.35, swede root 0.41 and turnip root 0.51 % of DM.

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*Manuscript received January 1991*



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## SELOSTUS

### Viljelykasvien kadmium- ja rikkipitoisuuksien vertailu


MIKKO SILLANPÄÄ ja HÅKAN JANSSON

Maatalouden tutkimuskeskus



Yhdeksällä koepaikalla eri puolilla Suomea rinnakkain kasvaneiden 16 viljelykasvin ja niiden eri osien kadmium- ja rikkipitoisuudet analysoitiin ja verrattiin.

Korkeimmat todetut keskimääräiset kadmiumpitoisuudet (sokerijuurikkaan naateissa) olivat noin satakertaisia verrattuna alhaisimpiin (herneen siemenet). Myös saman kasvin

eri osien välillä oli huomattavia eroja.

Yleensä viljakasvien jyvissä oli kadmiumia vähän. Laidunkasvien kadmiumpitoisuudet olivat samaa tasoa kuin viljakasvien jyvissä tai sitä korkeampia, mutta alhaisempia kuin korsissa. Tehokkaimmiksi kadmiumin kerääjiksi osoittautuivat juurikasvit, joiden sekä juurien että naattien kadmiumpitoisuudet olivat keskimäärin selvästi muita kasveja korkeampia.

Eri kasvien rikkipitoisuudet vaihtelivat vähemmän kuin niiden kadmiumpitoisuudet. Suurimmat mitatut rikkipitoisuudet lantun naateissa ylittivät vastaavat keskimääräiset pitoisuudet sokerijuurikkaan juurissa 18-kertaisesti. Myös kasvien sisäinen rikkipitoisuuksien vaihtelu oli vähäisempää. Lanttu ja rypsi osoittautuivat tehokkaimmiksi rikin kerääjiksi, mutta myös nauriin juuresta, herneen varsista ja sipulista mitattiin korkeita rikkipitoisuuksia. Vähiten rikkiä sisälsivät sokerijuurikkaan ja porkkanan juuret. Myös viljakasvit ja timotei heinä-asteella olivat melko rikkiköyhiä. Raiheinä sisälsi heinäkasveista eniten rikkiä.

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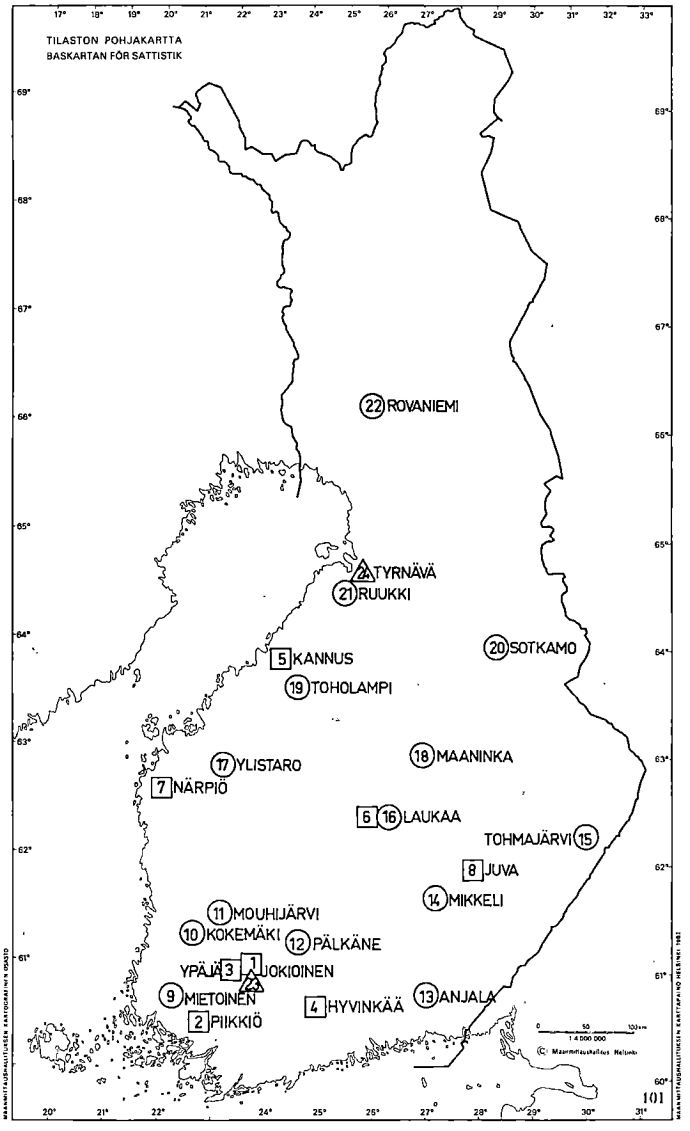


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