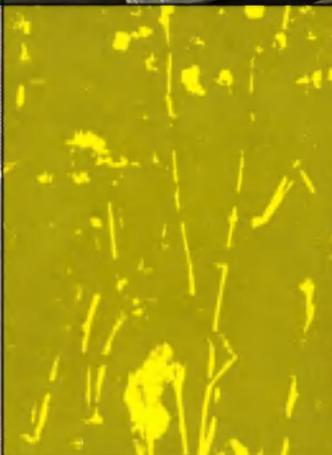
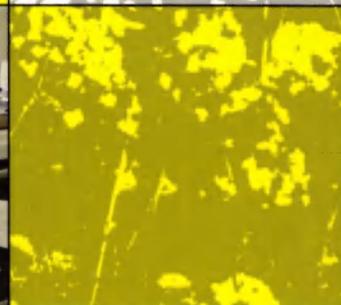




# 100th anniversary of IB 1990

papers on current research



**institute for soil fertility research (IB)  
haren - the netherlands**

# 100th Anniversary of IB 1990

Papers on current research

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# **The Institute for Soil Fertility Research 1890-1990**

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## **Abstract**

The Institute for Soil Fertility Research in Haren, the Netherlands, was established as a State Agricultural Experimental Station in Groningen on 2 January 1890. From 1890-1915 the major occupation of the experimental station was the quality control of animal feedstuffs and fertilizer materials for agriculture in the northern part of the Netherlands. In 1916, the experimental station was given the task to conduct scientific research on arable and grassland farming in the Netherlands. The research areas after 1916 can be distinguished into (1) soils and hydrology, (2) soil fertility and fertilizers, and (3) crops and crop production. Of these research areas, only soil fertility and fertilizers is still within the domain of the present Institute for Soil Fertility Research. The other research areas have been transferred to existing (soils) or newly founded institutions (hydrology, crops, crop production). The research on the 'fertility factors' laid the foundation for the system of fertilizer recommendations in the Netherlands, on the basis of soil analysis. In recent years, research emphasis has shifted to environmental issues and the ecology of agricultural systems, making use of simulation modelling and other mathematical tools for the description of soil-crop ecosystems.

## **Introduction**

The roots of the Institute for Soil Fertility Research in Haren, the Netherlands, go back to the State Agricultural Experimental Station in Groningen, the Netherlands, which was officially opened on 2 January 1890. The editorial board of the Netherlands Journal of Agricultural Science (NJAS) has kindly agreed to devote a special issue to soil fertility research, to mark the centennial of the institute.

The present paper gives a brief overview of the history of the Institute for Soil Fertility Research, thus placing the scientific research reported in this issue of NJAS in a historical context. The information on which the present paper is based, was derived from a book entitled 'Institute for Soil Fertility Research 1890-1990' (Harmsen, 1990). As most of the original references are not readily available to readers outside the Netherlands, no further references will be given in the present paper. The interested readers in the Netherlands are referred to Harmsen (1990).

## **The system of State Agricultural Experimental Stations in the Netherlands**

The origin of the Agricultural Experimental Stations in Western Europe goes back to the mid-nineteenth century, when experimental stations were established in England (Rothamsted, 1840), Germany (1850), France (1868), and Belgium (1872). In the Netherlands, the efforts of **Adolf Mayer** (1843-1942), at the time teacher in

agricultural chemistry at the State Agricultural College in Wageningen, resulted in the establishment of the first Agricultural Experimental Station in Wageningen, on 1 February 1877. It was established to meet the demand for research on fertilizers, animal feedstuffs and seeds, to inform the farmers on the use of these materials, and to assist the farmers whenever they needed scientific advice. In practice, there was mainly a need for quality control of fertilizers, animal feedstuffs and seeds, and soon the chemical (and botanical) analysis of these materials became the major occupation of the experimental station.

It took several years before the government and the farmers' organizations were convinced of the need to establish a network of state experimental stations in the Netherlands. **Adolf Mayer** mentions in this connection that the farmers in the Netherlands were relatively prosperous in those days, that the distribution of the landownership was quite reasonable, and that the overseas colonies offered employment and opportunities to those who could not find suitable employment at home. Hence, the need to invest in agricultural research and quality control did not appear to be very urgent. Also, the liberal principles, which prevailed from the middle of the 19th century onwards, did not encourage state interference with what were considered private agricultural affairs.

However, in the late eighteen-seventies, the supply of large quantities of low-priced agricultural products from the United States of America on the European markets led to a steep decline in the prices of these commodities, which affected the Dutch farmers in particular, as they were strongly dependent on the export of their products. The resulting agricultural crisis exposed a serious weakness of Dutch agriculture at that time: during the past decades, there had been insufficient attention to scientific developments and innovative technologies in agriculture. As a result, Dutch agriculture had lost its leading position in Western Europe. Concern about the competitiveness of Dutch agriculture resulted in the establishment, in 1886, of a State Commission on Agriculture, headed by **C. J. Sickesz**. One of the recommendations of this commission was to establish experimental stations in the major agricultural regions of the Netherlands. This led to the establishment of State Agricultural Experimental Stations in Groningen, Hoorn and Breda in 1890. The experimental station in Breda moved to Goes in 1893, and a fifth experimental station was established in Maastricht in 1898. The department of quality control of seeds of the experimental station in Wageningen developed into an independent Agricultural Experimental Station for Seed Quality in 1899. Hence, by the turn of the century there were six experimental stations in the Netherlands: in Wageningen (2), Groningen, Hoorn, Goes and Maastricht.

Five of the six State Agricultural Experimental Stations were each responsible for a certain region of the Netherlands (Fig. 1), whereas the Agricultural Experimental Station for Seed Quality in Wageningen worked for the entire country. The experimental stations were responsible for agricultural research and for the quality control of fertilizers, animal feedstuffs and other materials, in their respective regions. Because of the growing demand for quality control, the experimental stations were unable to spend sufficient time on agricultural research. This unsatisfactory situation led to the reorganization of 1913-1915, when the experimental stations

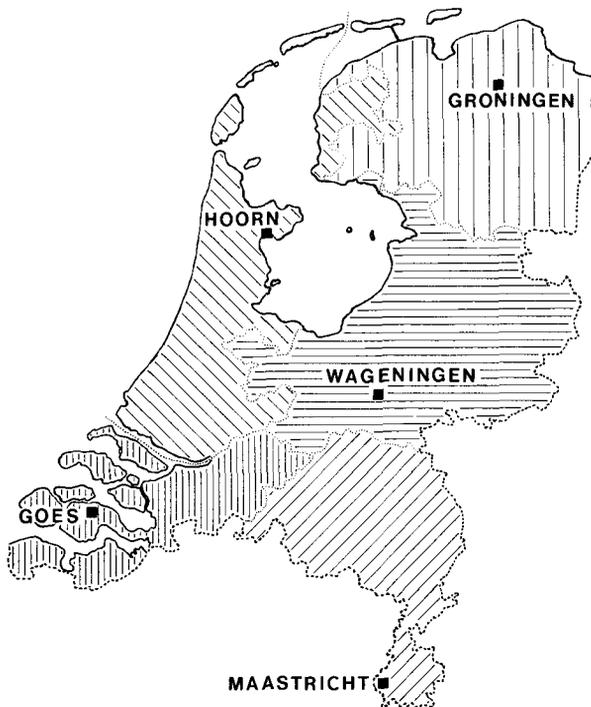


Fig. 1. Regions served by the five State Agricultural Experimental Stations around 1900.

were divided into stations for agricultural research (Groningen and Hoorn) and stations for quality control of fertilizers (Maastricht), animal feedstuffs (Wageningen), seed quality (Wageningen, as from 1899) and other materials, such as herbicides and fungicides (Goes). The experimental station in Groningen became responsible for agricultural research on arable crops and pastures, and the station at Hoorn for research on dairy products and animal feeding. For the history of the latter experimental station, see: Honing & Langelaar (1990).

As all experimental stations now had country-wide responsibilities, the rationale for the excentric location of most of these stations had ceased to exist. In the years following the reorganization of 1913-1915, most of the experimental stations moved to the center of the country (Wageningen or Lelystad) or were closed down. The State Agricultural Experimental Station in Goes (Fig. 2) was closed down in 1922, the experimental station in Hoorn moved to Lelystad in the mid-seventies and is now called Institute for Livestock Feeding and Nutrition Research (IVVO), whereas the experimental station in Maastricht moved to Wageningen in 1979 and merged to form a new institute in 1980, the State Institute for Quality Control of Agricultural Products (RIKILT). The experimental station in Groningen, however, remained in the north of the Netherlands and developed into the present Institute for Soil Fertility Research in Haren.



Fig. 2. In the early days of the experimental stations, staff members moved frequently from one station to the other. For example, four future directors at the experimental station in Groningen had previously worked at the station in Goes: Dr A. van Bijlert (1891-1893), Dr B. Sjollema (1893), Dr D. J. Hissink (1902-1906) and Ir J. G. Maschhaupt (1902-1907). The photograph shows the personnel of the experimental station in Goes, at the occasion of the departure of Dr D. J. Hissink as director of the station in 1906. In 1907, Dr D. J. Hissink was succeeded by Dr J. C. de Ruyter de Wildt, who had worked as a research chemist at the station in Groningen from 1904-1907. Photograph: front row, third from the left: Ir J. G. Maschhaupt; next to him: Dr D. J. Hissink.

Note: In the Dutch academic system, the title of 'Drs' (Doctorandus) refers to a person who has obtained a university degree, whereas the title 'Ir' (Engineer) refers to a degree obtained at a technical university. Both degrees are comparable to a M.Sc. degree. The titles 'Dr' and 'Prof.' have the same meaning as in the UK and USA systems.

### State Agricultural Experimental Station in Groningen (1890-1916)

The State Agricultural Experimental Station in Groningen was officially opened on 2 January 1890. The experimental station was accommodated in rented houses, at Nieuwe Ebbingestraat 26 (1889-1891) and Westersingel 5 (1891-1904), before it was moved to a new (own) building, at Prof. H. C. van Hallstraat 3 in Groningen, which was officially opened on 13 February 1904. This building was used by the experimental station until 1968, when new facilities in Haren became available.

The first director of the experimental station was **Dr A. F. Holleman**, who assumed his duties on 1 August 1889. Under the directorships of **Dr A. F. Holleman**

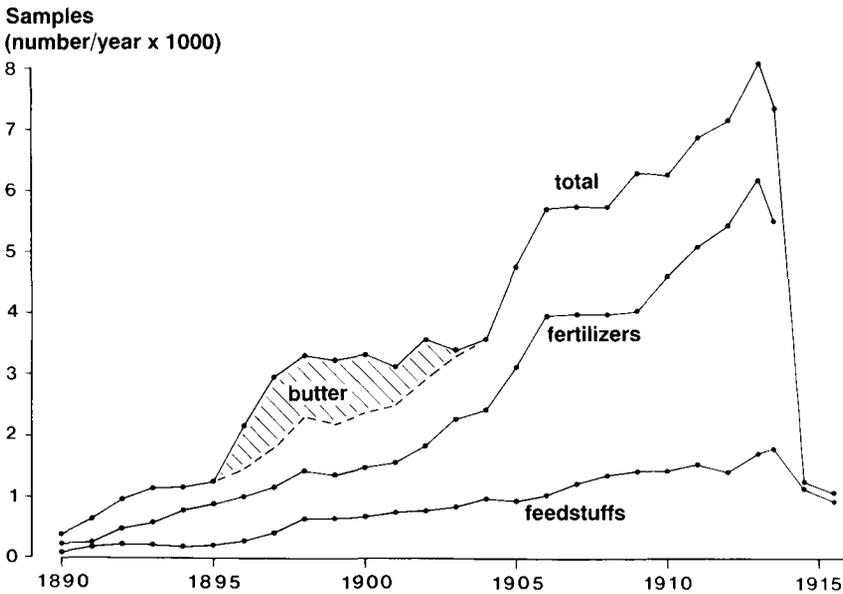


Fig. 3. Numbers of samples of animal feedstuffs, fertilizers and butter, and the total number of samples that were analysed annually by the State Agricultural Experimental Station in Groningen during 1890-1915.

(1889-1893), **Dr A. van Bijlert** (1894-1895), **Dr B. Sjollema** (1895-1907) and **Ir J. G. Maschhaupt** (1907-1916), the core staff of the experimental station increased from 3 in 1890 to 27 by the end of 1916.

The major occupation of the State Agricultural Experimental Station consisted of the chemical analysis of fertilizer materials, animal feedstuffs and butter samples. The total number of samples that were analysed increased from 21 during the last two months of 1889 to about 8000 in 1913 (Figs. 3-4). From 1903-1904 onwards, the analysis of butter samples was taken over by the newly established State Dairy Station at Leiden. As part of a reorganization of the State Agricultural Experimental Stations in the Netherlands, the analysis of fertilizer samples was taken over by the experimental station in Maastricht as from 1 May 1914, and the analysis of animal feedstuffs by the experimental station in Wageningen as from 1 May 1916.

The experimental stations had a dual task: quality control and scientific research. Because of the large (and ever increasing) numbers of samples to be analysed, and the limited resources of the experimental stations, the scientific research program did not develop as well as had been hoped for when the experimental stations were established. However, some scientific research was conducted by the experimental stations.

The emphasis in the research program in Groningen was on soils, soil fertility, and fertilizers. One of the most important lines of research was the research on the so-called 'soil diseases', that is, micronutrient-deficiencies induced by low (magnesi-



Fig. 4. Inside the analytical laboratory of the experimental station.

um) or high (manganese) pH. This research was started around 1908 by **Dr B. Sjollema** and **Ir J. Hudig**, and was continued by the latter, together with **C. Meijer**.

Although the emphasis in Groningen was on soils, soil fertility and fertilizers, the area covered by the research program of the experimental station was very broad in those days and included the quality and cultivation of arable crops and grassland (including rooting studies), plant nutrition, rainwater quality, hydrology, soils and soil fertility, and fertilizers, including animal manures.

#### **State Agricultural Experimental Station for Arable and Grassland Farming (1916-1939)**

Following the reorganization of 1913-1915, the experimental station in Groningen was renamed State Agricultural Experimental Station for Arable and Grassland Farming (Fig. 5). Its task was to conduct research and experiments on arable and grassland farming. The emphasis was on three lines of research: (1) soils and hydrology, (2) soil fertility and fertilizers, and (3) production and quality of crops.

As from 1 May 1916, the experimental station was divided into five independent research departments, each of them headed by a 'director'. Together the directors of the research departments formed the 'Board of Directors' and appointed each year a chairman and a secretary from their midst. The research departments and



Fig. 5. The staff of the experimental station in 1916. Front row, sixth from the left: Ir. J. G. Maschhaupt; behind him, to the left: Ir. J. Hudig.

their directors were:

1. Department for crop production on clay and sandy clay soils — **Ir J. G. Maschhaupt** (1916-1930).
2. Department for crop production on sandy and peat soils — **Ir J. Hudig** (1916-1930).
3. Department for general soil research — **Dr D. J. Hissink** (1916-1926).
4. Department for bacteriological research — **Dr N. L. Söhngen** (1916-1918), **Dr F. C. Gerretsen** (1919-1930).
5. Department for botanical research — **Dr K. Zijlstra** (1916-1930).

After this reorganization, the 1st and 2nd departments remained in the main building of the experimental station, at Prof. H. C. van Hallstraat 3 (Figs. 6-7). The 3rd department, later the Institute of Soil Science, was accommodated in a rented house at Herman Colleniusstraat 25, from 1930-1931 supplemented by a house at Jozef Israëlsstraat 42. In July 1931 the Institute of Soil Science moved to a new (own) building, at Verlengde Oosterweg 122 in Groningen (Fig. 8). This building was used until 1968, when new facilities in Haren became available. The 4th department was accommodated in a rented house at Wassenberghstraat 19, whereas for the 5th department initially no facilities were available, forcing **Dr K. Zijlstra** to use some space in his own house for his botanical work. When **Dr N. L. Söhngen** left for Wageningen in 1918, **Dr K. Zijlstra** moved to the Wassenberghstraat, with the



Fig. 6. The main building of the experimental station at Prof. H. C. van Hallstraat 3 in Groningen. Wooden building to the left: Laboratory for Soil Testing.



Fig. 7. The experimental grounds adjacent to the main building. Front, to the right: lysimeters.

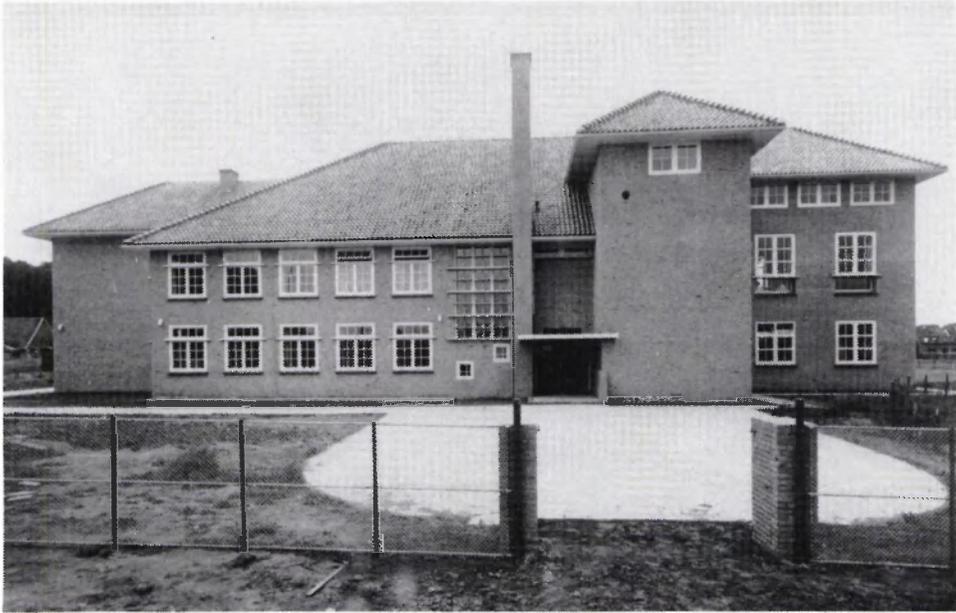


Fig. 8. The building of the Institute of Soil Science at Verlengde Oosterweg 122 in Groningen.

result that no space was available for **Dr F. C. Gerretsen** when he arrived in Groningen in 1919. This unsatisfactory situation came to an end when both departments moved to a large (rented) house at Eemskanaal ZZ 1, a building that was used until 1968 (Fig. 9).

The 3rd department for general soil research became an independent institute in 1926, the Institute of Soil Science in Groningen, which remained independent until 1939, when **Dr D. J. Hissink** retired as director of the institute. Soil research developed strongly under the directorship of **Dr D. J. Hissink**. The main emphasis was on physicochemical soil research, but under the leadership of **Dr S. B. Hooghoudt** hydrological research also gained importance. Much research was done on the soils reclaimed from the 'Zuiderzee'. The physicochemical and hydrological knowledge about these soils helped to prepare the 'polders' for cultivation.

The four research departments (other than the soils department) of the experimental station remained autonomous until October 1930, when they were united under one 'general' director, **Prof. Dr O. de Vries**. After the departure of **Ir J. Hudig** to Wageningen in 1931, the 1st and 2nd departments were reorganized and two new departments were formed: a chemical department, headed by **Ir J. G. Maschaupt**, and an agronomic department, headed by **Ir P. G. Meijers**.

The most important line of research, in terms of impact on agriculture in the Netherlands, was probably the research on soil fertility and fertilizers, commonly referred to as the research on the 'fertility factors'. The notion of 'fertility factor' refers to a quantifiable soil property that may affect soil productivity (i.e. crop yields). Examples of fertility factors are the lime and potash status of soils, but also



Fig. 9. The building at Eemskanaal ZZ 1 in Groningen, where the 4th and 5th departments of the experimental station were housed.

the cation-exchange capacity, moisture-storage capacity, micronutrient availability, etc.

Although soil fertility research can be traced back to **Dr A. F. Holleman** and **Dr B. Sjollema**, the breakthrough came in the mid-twenties, when it was shown that the occurrence of the so-called 'soil diseases' depended on the lime status of the soil. The lime status of a soil was expressed as the lime index, which is a measure of the

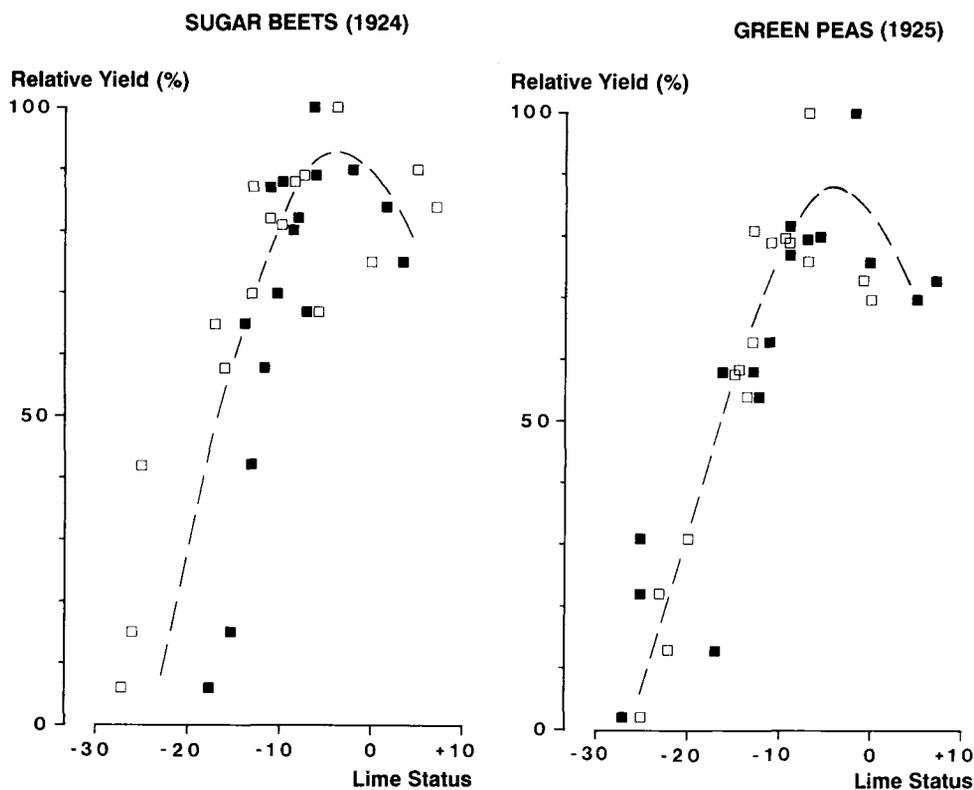


Fig. 10. Relative yields of sugar beet in 1924 (left) and green peas in 1925 (right) as a function of the lime status of the soil at the experimental field at Spitsbergen, Netherlands. The lime status is indicated by an index, which ranged from about  $-30$  (pH about 4.1) to  $+10$  (pH about 7.3) under the conditions of the experiment. Open symbols ( $\square$ ) refer to the lime status at the start of the season, closed symbols ( $\blacksquare$ ) to the lime status after harvest.

amount of lime needed to reach a pH of 6.5. In experiments with sugar beet (1924) and green peas (1925) at Spitsbergen, the Netherlands, **Ir J. Hudig** and **C. Meijer** showed that crop yields increased with increasing lime index up to a maximum (or: optimum) yield at lime-index values between  $-10$  (pH about 5.7) and  $0$  (pH about 6.5), and thereafter decreased with increasing lime index (Fig. 10). The low yields at low lime index were later shown to be caused by magnesium deficiency at low pH, whereas the low yields at high lime index were shown to be due to manganese deficiency at high pH.

The research was not limited to the lime status of soils, but included other fertility factors, such as the potash status and the phosphate status, as well. In many cases 'optimum curves', similar to the ones shown in Figure 10, were obtained when relative yields were plotted as a function of a particular fertility factor. This led to the concept in which yield was considered to be a function of a number of (interacting)

fertility factors. The methodology of the research on the fertility factors was largely developed under the directorship of **Prof. Dr O. de Vries**. The scientists involved in this research included **Drs P. Bruin, Dr Ir H. J. Frankena, Dr F. van der Paauw** and **Ir W. C. Visser**.

The research on the lime status derived its practical significance from the fact that the 'soil diseases' were widespread in those days and that it was now shown that farmers could overcome these 'soil diseases' by either liming their soils, at low pH, or applying an acidifying fertilizer, such as ammonium sulfate, at high pH. As a result of these findings, the demand for soil analysis by farmers increased strongly in the early twenties. As the experimental station was not equipped for such large numbers of routine analyses, the director of the 2nd department, **Ir J. Hudig**, took the initiative to establish a laboratory for soil testing on a commercial basis. This resulted in the foundation, in 1927, of the Laboratory for Soil Testing (BLG) in Groningen. The director of the 2nd department became also director of the laboratory, until 1930, when the general director, **Prof. Dr O. de Vries**, formally took over this responsibility. In practice, however, it was **Ir F. J. A. Dechering** who was in charge of the operations of the laboratory. The Laboratory for Soil Testing was housed in a building on the grounds of the experimental station at Prof. H.C. van Hallstraat in Groningen (Fig. 6). After 1945 the head office of the laboratory moved to Oosterbeek, and in 1965 the establishment in Groningen closed down.

The research on the fertility factors laid the foundation for the fertilizer recommendations in the Netherlands, on the basis of soil analysis. In its present form, this system of fertilizer recommendations considers such factors as soil nutrient status (soil analysis), soil type, type of crop, cropping history, crop residue management and the use of animal or green manures. Although in recent years the use of fertilizers in agriculture has been in discussion, the existing system of fertilizer recommendations is still one of the more advanced systems in Europe and has contributed significantly to the rise of agriculture in the Netherlands after the second world war.

### **Agricultural Experimental Station and Institute of Soil Science (1939-1957)**

In 1939, a reorganization took place, which led to the separation of soil and soil fertility research on the one hand, and crop and crop production research on the other. In the course of 1939 the Central Institute for Agricultural Research (CILO) was established in Wageningen and this institute took over the tasks (as well as the staff) of the experimental station in Groningen in the field of crop and crop production research. In 1956, the CILO terminated its activities and its staff was divided over three newly founded institutions in Wageningen: the Institute for Biological and Chemical Research on Field Crops and Herbage (IBS), the Experimental Station for Arable and Grassland Farming (PAW) and the Institute for Research on Storage and Processing of Agricultural Products (IBVL). In 1970, the PAW was moved to Lelystad and split up into two new stations: the Experimental Station for Cattle, Sheep and Horse Husbandry (PR) and the Experimental Station for Arable Farming (PA). The IBS merged to form the Center for Agrobiological Research (CABO) in Wageningen (1975), the PA merged to form the Experimental Station for Arable

Farming and Field Production of Vegetables (PAGV) in Lelystad (in 1976), and the IBVL merged to form the Institute for Agrotechnological Research (ATO) in Wageningen (1989). Hence, the research on the production, storage and quality of crops, conducted by the experimental station in Groningen until 1939, is at present divided over the research programs of four institutions: CABO and ATO in Wageningen, and PR and PAGV in Lelystad.

The Institute of Soil Science, which had been independent since 1926, was reunited with the experimental station in 1939 and the new institution was renamed 'Agricultural Experimental Station and Institute of Soil Science'. In 1945 this institution became part of the Netherlands Organization for Applied Scientific Research (TNO) and the name was changed into 'Agricultural Experimental Station and Institute of Soil Science TNO'.

In 1939, a cooperative agreement was concluded between the experimental station in Groningen and the Directorate of State Mines (DSM) in Limburg. This agreement arranged for the appointment of **Dr Ir E. G. Mulder** at the experimental station in Groningen. His task was to investigate the role of nitrogen in arable and grassland farming. The cooperation between the experimental station and the DSM went back to the early thirties, when **C. Boudewijn**, director of the Agricultural Bureau of the State Mines, took the initiative to establish a number of experimental fields to test nitrogen fertilizers throughout the country. After World War II, the cooperation between the fertilizer industry, by then organized in the Netherlands Fertilizer Institute (NMI), and the experimental station was continued and, in fact, strengthened. In 1956, **Dr Ir E. G. Mulder** became professor of microbiology at the Wageningen Agricultural University and he was succeeded at the experimental station in Groningen by **Dr Ir P. F. J. van Burg**. In 1964, a second scientist, **Dr Ir K. Dilz**, was placed by the fertilizer industry at the experimental station. In 1974, **Dr Ir P. F. J. van Burg** became director of the NMI. He was succeeded at the experimental station by **Dr Ir W. H. Prins**. At present, the scientific staff of the NMI-establishment in Haren consists of **Dr O. Oenema** (head) and **Ir P. J. van Erp**.

The research departments that had been autonomous during 1916-1930 and united under one general director during 1930-1939, disappeared gradually during the period 1939-1957 and were replaced by a project-oriented research organization. In 1945, **Prof. Dr O. de Vries** left the institute and was succeeded by **Drs P. Bruin** as acting general director. The Laboratory for Soil Testing became independent and **Ir F. J. A. Dechering** became its director.

As for soil fertility and fertilizer research, the period 1939-1957 may be considered a period of extension and intensification of the research into the fertility factors. Areas on which research was focussed, or new areas of research, included the role of micronutrients, organic matter turnover in soils, the nitrogen cycle in agricultural systems, and soil physical properties and soil structure.

### **Institute for Soil Fertility Research (1957-1990)**

In 1956 the Institute for Land and Water Management Research (ICW) was established in Wageningen and the hydrological research of the experimental station in

Groningen was transferred (including the staff) to the newly founded institute in Wageningen. The Agricultural Experimental Station and Institute of Soil Science TNO became a foundation of the Ministry of Agriculture and Fisheries in 1957, and the name of the institution was changed into Institute for Soil Fertility Research. In 1958 the fertilization research for horticulture was transferred to the Institute for Soil Fertility Research.

In 1967, **Drs P. Bruin** retired as director of the Institute for Soil Fertility Research. In the same year he received a honorary doctor's degree from the Justus-Liebig University in Giessen, West-Germany. He was succeeded by **Ir C. M. J. Sluijsmans**, who remained director until 1985, when he stepped down as director, for health reasons. **Ir C. M. J. Sluijsmans** remained at the institute as a research scientist in the department of fertilization and plant nutrition, until his early retirement in 1987. He was succeeded by **Dr P. J. Lont** as acting director of the institute, until the new director, **Dr Ir K. Harmsen**, assumed his duties in 1986.

After 12 years of preparation, the new facilities of the institute were finally ready in 1968, thus putting an end to an almost continuous state of housing problems, which had started in 1916, with the foundation of the five research departments of the experimental station. In 1968 the institute moved from its three locations, that is, Prof. H. C. van Hallstraat 3, Eemskanaal ZZ 1 and Verlengde Oosterweg 122, to the new facilities at Oosterweg 92 in Haren (Fig. 11).

The period after 1957 may be considered a period of consolidation of the research into the fertility factors. There were also new lines of research, however, in particular in the field of environmental quality and soil ecology.



Fig. 11. Scale-model of the new building in Haren.

## Research outlook

In the past decades, the main objective of soil fertility research was to increase crop production levels and to meet specified crop quality standards. The research on the 'fertility factors' laid the foundation for the system of fertilizer recommendations in the Netherlands, on the basis of soil analysis. This research helped to promote the rational use of fertilizers in the Netherlands, which is now one of the highest in the world, on a per-hectare basis.

Traditionally, soil fertility and fertilization research paid attention to the fraction of the (applied) nutrients that ended up in the crop, thus contributing to higher yields or better quality, but largely ignored the fraction of nutrients not taken up by the crop, that is, stored in the soil or lost from the soil through volatilization, leaching or surface runoff. Hence, soil fertility research focussed on establishing correlative relationships between fertility factors or fertilizer application on the one hand, and crop quality or yield on the other, but did not consider the fate of nutrients not taken up by the crop. From an environmental point of view, however, the latter fraction is the important one, as it determines whether contamination of the environment or undesired effects on the soil biosphere may occur.

Although the emphasis in the research program was on agricultural production, the Institute for Soil Fertility Research has paid attention to environmental issues since the mid-sixties, long before these issues ranked high on the political agenda. For example, the 1970 Annual Report is devoted almost entirely to environmental issues and contains contributions by **Dr A. J. de Groot** on heavy metals in river sediments, by **Ir G. J. Kolenbrander** on the eutrophication of surface waters by nitrogen and phosphate, and by **Ir L. C. N. de la Lande Cremer** on the expected surpluses of animal manures as a result of intensive animal husbandry.

In 1987 the research task of the Institute for Soil Fertility Research was changed to the effect that the institute had to (1) strengthen its biological research program, (2) redirect its research in the field of fertilization and soil fertility, i.e., pay more attention to the environmental impact of the use of fertilizers, and (3) make more use of simulation modelling and other mathematical techniques for the description of soil-crop ecosystems. This redirection of the research program was part of a reorganization of agricultural research in the Netherlands, as laid down in the 'Development Plan for the Institutes and Experimental Stations of the Ministry of Agriculture and Fisheries, 1987-1990'. The present research program of the Institute for Soil Fertility Research requires a systems approach, making use of quantitative-analytical methods of research, in order to integrate disciplinary knowledge (physics, chemistry, biology, soil and crop sciences) as well as areas of application: agricultural production, environmental quality, and soil ecology.

The changes in research emphasis at the Institute for Soil Fertility Research in recent years should be viewed against the background of changing economic prospects for agriculture and an increasing public concern about the quality of the environment. The economic prospects for agriculture have changed in the sense that there are now surpluses of many agricultural commodities within the European Community, and it seems that further economic growth has to come from better quality and

diversification of products, rather than from higher production levels and more (of the same) products. The public concern about the quality of the environment has led the government to release a number of policy documents, such as the 'National Environmental Policy Plan', which sets environmental aims to be achieved in the next decade(s) and outlines ways of achieving these aims.

In the future research program of the Institute for Soil Fertility Research, mathematical modelling of soil-crop ecosystems will play an important part. The areas of application of the research, that is, agricultural production, environmental quality, and soil ecology, have to be integrated into multidisciplinary research projects. The main objective of the future research program will be to contribute to the development of agricultural systems that are sustainable, safe (for humans and the environment) and economically competitive. The word 'sustainable' is defined here as 'not resulting in any irreversible changes in the (potential) functioning of the soil and not leading to contamination of air or water beyond specified (permitted) levels'. The concept of sustainability will be a leading principle in the future research program. Sustainability is also important on a national scale: decreasing losses of nutrients to the atmosphere and the North Sea, balancing the import (e.g., animal feedstuffs) and the export of nutrients (e.g., meat and dairy products), and recycling nutrients where possible (e.g., animal manures, sewage sludges).

In the past, the Institute for Soil Fertility Research has helped to overcome nutrient deficiencies in Dutch agriculture and to increase production and product quality to their present levels. The challenge now is to maintain a competitive agriculture while preserving the environment.

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# **Modelling organic matter dynamics in different soils**

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## **Abstract**

A mathematical model was developed to describe carbon (C) and nitrogen (N) cycling in different types of soil, e.g. clay and sandy soils. Transformation rates were described by first-order kinetics. Soil organic matter is divided into four fractions (including microbial biomass pool) and three fractions of residues. The fraction of active soil organic matter was assumed to be affected by the extent of physical protection within the soil, so was the soil microbial biomass. The extent of protection influenced the steady state level of the model, and, hence, the mineralization rates. The mineralization rate in fine-textured soils is lower than in coarse-textured soils; in fine-textured soils a larger proportion of the soil organic matter may be physically protected. The availability of organic materials as a substrate for microorganisms is not only determined by their chemical composition, but also by their spatial distribution in the soil. In future research, attention will be paid to the effects of soil structure and soil texture and to the spatial distribution of organic materials and their decomposers.

*Keywords:* model, soil organic matter, protection, mineralization

## **Introduction**

Part of the nitrogen demand of plants is satisfied by uptake of inorganic nitrogen produced by mineralization of organic nitrogenous compounds in soil. The rate of mineralization depends on environmental conditions, such as moisture and oxygen status, carbon dioxide pressure, aeration, pH, temperature (Swift et al., 1979), but also on soil type and agricultural practices, such as crop rotation and cultivation. The efficiency of mineralized nitrogen as part of the nitrogen supply of plants is at a maximum when the timing of release from organic matter is synchronized with that of plant uptake. Thus, to optimize management of nitrogen supply in agricultural systems, understanding of the dynamics of soil organic nitrogen turnover is necessary.

Mechanistic dynamic simulation models have proven to be useful for the study of soil organic matter dynamics; they help to integrate the fragmentary knowledge about the processes involved and therefore to develop a better understanding of the behaviour of the soil system as a whole. They are useful in formulating and testing

hypotheses and in establishing the relative importance of parameters.

Most models on soil organic matter distinguish different pools, each representing material with a different stability with regard to decomposition (Parnas, 1974; Jenkinson & Rayner, 1977; Frissel & van Veen, 1981; Paustian, 1987). Although adequate methods to experimentally establish the partitioning of soil organic matter over these different pools are still lacking, this approach seems the most promising to describe soil organic matter dynamics on a field scale (Jenkinson & Rayner, 1977).

Differences in total net mineralization of labelled substrates between soils of different texture have been observed (Sorensen, 1981; van Veen et al., 1985). Net mineralization and immobilization are more rapid in sandy soils than in clay soils (Hassink, unpublished), and, generally, soils with a higher clay content have a higher organic matter content (Kortleven, 1963). The lower net mineralization in clay soils which leads to a higher organic matter content, is assumed to be caused by physical protection of soil organic matter and microbial biomass. Indications that soil particles provide protection against microbial decomposition are obtained from the observed large differences between turnover rate of particular compounds in liquid microbial cultures and in soils (van Veen & Paul, 1981), and indirectly from data showing that disruption of soil results in an increase in mineralization of both carbon and nitrogen (Gregorich et al., 1989). Apparently, the protection of part of the organic matter against microbial attack is lowered by the disruption of the soil. Sorensen (1975) already observed that the extent of protection varied with the degree of aggregation and clay content. The stabilizing effect is assumed to be the result of adsorption of organic material by layers in swelled clays, adsorption on the surface of silt and clay particles, or aggregate formation, which renders the organic material less accessible to decomposition by microorganisms.

We designed a computer model to simulate soil organic matter dynamics based on the models of van Veen (van Veen & Paul, 1981; van Veen et al., 1984; van Veen et al., 1985) as a first step toward simulating the effects of soil type on nitrogen mineralization. Most published models are used to describe and simulate field situations. The purpose of the present study is to analyse and explain model behaviour, with respect to both short-term and long-term effects, in order to increase insight in soil organic matter dynamics. Attention is paid to several aspects:

- carbon (C) and nitrogen (N) cycling in the soil,
  - the role of native soil organic matter and added organic material in soil fertility and nitrogen availability to the crop,
  - identification of key soil properties that would allow to differentiate between mineralization and immobilization of different soil types (clay and sandy soils).
- The final goal of the model is to predict (daily) net mineralization of different soils.

### **Model description**

Figure 1 shows the flow chart of the model. The main partition of organic matter is over recently added organic materials such as crop residues and manure, and native soil organic matter. Both are further subdivided into different components.

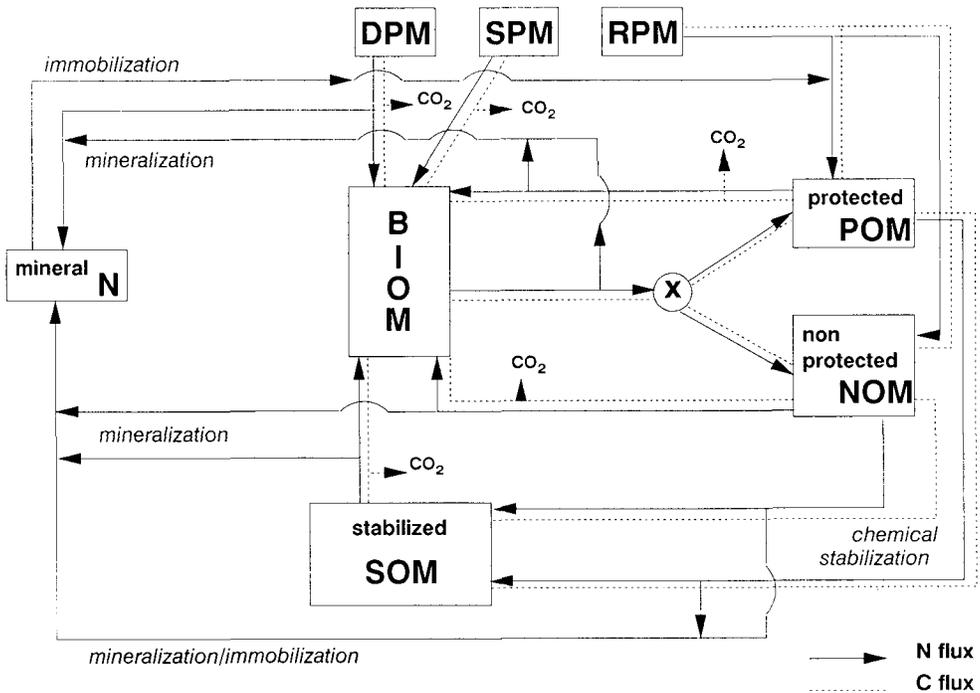


Fig. 1 Flow-chart of the model. The state variables (DPM: decomposable material, SPM: structural material, RPM: resistant material, BIOM: microbial biomass, POM: protected soil organic matter, NOM: nonprotected soil organic matter, SOM: stabilized soil organic matter), which characterize and quantify all properties that describe the state of the system, are represented by rectangles and the flows of material by solid (nitrogen) and dotted (carbon) lines.

*Residues*

Residues are considered to consist of three fractions each with its own resistance to biological decomposition (van Veen & Paul, 1981):

- (1) decomposable material (DPM), i.e. carbohydrates and proteins,
- (2) structural material (SPM), i.e. cellulose and hemicellulose,
- (3) resistant material (RPM), i.e. lignified structural material.

Each fraction is assumed to have a fixed carbon:nitrogen ratio ( $(C/N)_{dpm}$ ,  $(C/N)_{spm}$  and  $(C/N)_{rpm}$ ). The overall C/N ratio of the residue is the weighted mean of the three fractions. A high fraction of decomposable material ( $F_{dpm}$ ) results in a low overall C/N ratio, a high fraction of structural ( $F_{spm}$ ) and/or resistant material ( $F_{rpm}$ ) in a high value.

Decomposable and structural material (DPM, SPM) are considered to be decomposed by the microbial biomass, while the lignin fraction (RPM) directly enters the soil organic matter pool. This enables the description of the role of ligneous compounds in the chemical stabilization of organic matter in soil (Swift et al., 1979).

*Soil organic matter*

Soil organic matter is divided into three major fractions (Fig. 1): microbial biomass (BIOM), active organic matter (POM plus NOM) and stabilized organic matter (SOM), an old inactive fraction stabilized by unspecified mechanisms (van Veen et al., 1984).

Active organic matter is divided into a physically protected component (POM) and a nonprotected component (NOM). As protection against decomposition appears more effective in soils with a high clay and silt content (lower nitrogen mineralization (Hassink, unpublished), in these soils a higher protection of the active soil organic matter is assumed to be physically protected.

*Microbial biomass*

Soil microbial biomass is also divided into a protected and a nonprotected component (van Veen et al., 1984). It is assumed that each soil has a specific maximum capacity to protect microorganisms, which is roughly equal to the size of the microbial biomass present in a soil not recently disturbed, e.g. by tillage or large additions of fresh organic material. Microbial biomass has been shown to be positively correlated with total organic carbon (Schnurer et al., 1985; Theng et al., 1989), and therefore, the maximum capacity to protect microorganisms ( $C_{B,max}$ ) is defined as a fraction of the total organic soil carbon ( $C_T$ ) (Theng et al., 1989). Evidence for the existence of such a maximum protective capacity is derived from the common observation of a sharp increase in microbial biomass upon addition of carbon compounds, followed by a steep decline to the original level (van Veen et al., 1984). In the model, we assume that the microbial biomass in excess of the maximum protective capacity of the soil is subject to rapid turnover, whereas the protected microbial biomass is assumed to have a hundredfold lower turnover time.

$$C_B \geq C_{B,max} : \begin{matrix} C_{B,P} = C_{B,max} \\ C_{B,n} = C_B - C_{B,max} \end{matrix} \quad (1)$$

$$C_B \leq C_{B,max} : \begin{matrix} C_{B,P} = C_B \\ C_{B,n} = 0 \end{matrix} \quad (2)$$

where  $C_B$  = total microbial biomass,  $C_{B,n}$  = nonprotected microbial biomass, and  $C_{B,P}$  = protected microbial biomass.

*Carbon and nitrogen fluxes*

All transformations are considered to be first-order reactions, on the assumption that the concentration of the material involved rather than the biological capacity is rate-limiting in decomposition (van Veen & Paul, 1981).

This implies that the rate of substrate decomposition  $D_C$  ( $\text{kg C ha}^{-1} \text{ d}^{-1}$ ) is

proportional to the amount of substrate  $C_s$  (kg C ha<sup>-1</sup>):

$$D_C = \frac{dC_s}{dt} = k \times C_s \quad (3)$$

Where  $k$  is the first-order decomposition rate constant (d<sup>-1</sup>) and  $t$  is time (d).

Each transformation indicated in Figure 1 has a specific decomposition rate constant ( $k$ ) and a yield efficiency factor ( $E$ ), defining the fraction of the decomposing material incorporated into microbial biomass  $C_B$  (kg C ha<sup>-1</sup>). The remainder ( $1 - E$ ) leaves the system as CO<sub>2</sub>. The growth rate of microbial biomass,  $G_C$  (kg C ha<sup>-1</sup> d<sup>-1</sup>), and the rate of respiration (kg C ha<sup>-1</sup> d<sup>-1</sup>) are described by:

$$G_C = \frac{dC_B}{dt} = E \times k \times C_s \quad (4)$$

$$\frac{dCO_2}{dt} = D_C - G_C = (1 - E) \times k \times C_s \quad (5)$$

The decomposition rate constants ( $k$ ) and efficiency factors ( $E$ ) are assumed to be independent of the kind of residue and soil type. It is outside the scope of this study to investigate the effects of all environmental factors like temperature, soil moisture content, gaseous atmosphere composition, soil pH, and their interactions. Suboptimal conditions are taken into account using reduction factors for the rates of decomposition, with values between 0 (complete inhibition) and 1 (optimum conditions) (van Veen & Paul, 1981).

The rates of decomposition for structural (SPM) and resistant (RPM) material are calculated as a function of the fraction of resistant material, according to Parton et al. (1987):

$$k_2 = k_{2m} \times \exp \left( -3.0 \times \frac{F_{rpm}}{F_{spm} + F_{rpm}} \right) \quad (6)$$

$$k_3 = k_{3m} \times \exp \left( -3.0 \times \frac{F_{rpm}}{F_{spm} + F_{rpm}} \right) \quad (7)$$

where  $k_{2m}$  and  $k_{3m}$  are the maximum relative decomposition rates for structural and resistant material, respectively. Both rates of decomposition decrease as the lignin component ( $F_{rpm}$ ) increases; that is based on the assumption that as the lignin component increases the accessibility, and thus the decomposability of structural materials such as hemicellulose and cellulose decrease rapidly (Swift et al., 1979). Lignin and (hemi)cellulose are closely related within cell walls and although there is probably no chemical interaction between the two, lignin is released as the microbes decompose (hemi)cellulose. The resistant material is distributed in a 1:1 ratio between the nonprotected (NOM) and the protected (POM) organic matter.

Decomposing microbial biomass is also distributed between the nonprotected and the protected organic matter; the actual distribution is governed by a soil-type

specific parameter  $\alpha_p$ . The proportion of carbon and nitrogen released during decomposition of dead microbial biomass, retained near protected organic matter is higher in clay soils than in sandy soils. Hence, the value of  $\alpha_p$  is higher for soils with a high clay content, resulting in a larger proportion of carbon and nitrogen from decomposing microbial biomass into the protected (POM) organic matter pool.

The nitrogen fluxes are assumed to be proportional to the carbon fluxes. The rate of nitrogen release  $D_N$  ( $\text{kg N ha}^{-1} \text{d}^{-1}$ ) thus depends on the C/N ratio of the substrate  $((C/N)_s)$ , whereas the growth rate of microbial biomass-N  $G_N$  ( $\text{kg N ha}^{-1} \text{d}^{-1}$ ) depends on the C/N ratio of the microbial biomass  $((C/N)_B)$ .

$$D_N = \frac{k \times C_s}{(C/N)_s} \quad (8)$$

$$G_N = \frac{E \times k \times C_s}{(C/N)_B} \quad (9)$$

If  $1/(C/N)_s > E/(C/N)_B$ , net mineralization ( $N_{\min} > 0$ ,  $\text{kg N ha}^{-1} \text{d}^{-1}$ ) occurs:

$$N_{\min} = k \times C_s \times \left( \frac{1}{(C/N)_s} - \frac{E}{(C/N)_B} \right) \quad (10)$$

In the reverse condition, net immobilization is the result.

### Model formulation

The concepts outlined so far result in the following equations for the rates of change of the different state variables.  $C_{\text{inp}}$  ( $\text{kg C ha}^{-1} \text{d}^{-1}$ ) is the (daily) residue input; all other symbols are explained in the preceding text, Figure 1, and Tables 1a and 1 b. The rate of decomposition of the various components of residues is described as (see (3)):

$$\frac{dC_{\text{dpm}}}{dt} = -k_1 \times C_{\text{dpm}} + F_{\text{dpm}} \times C_{\text{inp}} \quad (11)$$

$$\frac{dC_{\text{spm}}}{dt} = -k_2 \times C_{\text{spm}} + F_{\text{spm}} \times C_{\text{inp}} \quad (12)$$

$$\frac{dC_{\text{rpm}}}{dt} = -k_3 \times C_{\text{rpm}} + F_{\text{rpm}} \times C_{\text{inp}} \quad (13)$$

The rates of change in the amount of carbon in microbial biomass  $dC_B/dt$  ( $\text{kg C ha}^{-1} \text{d}^{-1}$ ), nonprotected soil organic matter  $dC_N/dt$  ( $\text{kg C ha}^{-1} \text{d}^{-1}$ ), protected soil organic matter  $dC_P/dt$  ( $\text{kg C ha}^{-1} \text{d}^{-1}$ ), and stabilized soil organic matter  $dC_S/dt$  ( $\text{kg C ha}^{-1} \text{d}^{-1}$ ), respectively, are described by:

$$\frac{dC_B}{dt} = E_1 \times k_1 \times C_{dpm} + E_2 \times k_2 \times C_{spm} + E_5 \times k_5 \times C_N + E_6 \times k_6 \times C_P + E_7 \times k_7 \times C_s - k_{4P} \times C_{B,P} - k_{4N} \times C_{B,n} \quad (14)$$

$$\frac{dC_N}{dt} = 0.5 \times E_3 \times k_3 \times C_{rpm} + (1 - \alpha_p) \times E_4 \times (k_{4P} \times C_{B,P} + k_{4n} \times C_{B,n}) - (k_5 + k_8) \times C_N \quad (15)$$

$$\frac{dC_P}{dt} = 0.5 \times E_3 \times k_3 \times C_{rpm} + \alpha_p \times E_4 \times (k_{4P} \times C_{B,P} + k_{4n} \times C_{B,n}) - (k_6 + k_9) \times C_P \quad (16)$$

$$\frac{dC_S}{dt} = E_8 \times k_8 \times C_N + E_9 \times k_9 \times C_P - k_7 \times C_s \quad (17)$$

### Parameter values

Standard values for model parameters are given in Table 1a (optimum temperature (25 °C) and moisture). Most of the parameter values are obtained from the literature (van Veen & Paul, 1981; van Veen et al., 1984; van Veen et al., 1985).

For transformations without microbial interference the yield efficiency factor is by definition 1. In the model this applies to the flow of resistant material to non-protected and protected organic matter ( $E_3 = 1$ ), the flow of microbial products to nonprotected and protected organic matter ( $E_4 = 1$ ), and the transformation of nonprotected and protected organic matter into stabilized organic matter ( $E_8 = 1$ ,  $E_9 = 1$ ).

Physical protection leads to a decrease in rate of decomposition. The rate of decomposition of protected microbial biomass ( $k_{4P}$ ) is set rather low: 0.005 d<sup>-1</sup> (inactive population with a relatively low maintenance requirement) and is of the same order of magnitude as the turnover time for microbial biomass used by Jenkinson & Parry (1989). Microbial biomass formed in excess of soil protection capacity is assumed to decompose at a much higher rate ( $k_{4n} = 0.5$  d<sup>-1</sup>, active population with a relatively high maintenance requirement). The rate of decomposition of protected organic matter ( $k_6$ ) is set at 0.03 times that of nonprotected organic matter ( $k_5$ ) on the basis of the results of simulation studies of the transformation of simple amino acids in soils (Paul & van Veen, 1978). Stabilized organic matter has a turnover time of the order of 1000 years or more, as indicated by <sup>14</sup>C-dating (Paul & van Veen, 1978).

The C/N ratios of the state variables are assumed to be constant. For decomposable material ((C/N)<sub>dpm</sub>) it is set at 6 (overall C/N ratio of carbohydrates and proteins), for structural material ((C/N)<sub>spm</sub>) at 150 (Parton et al., 1987), and for resistant material ((C/N)<sub>rpm</sub>) at 100 (lignified material, Whitmore & Parry, 1988). The

C/N ratio of microbial biomass ((C/N)<sub>B</sub>) is set at 8 (Hassink, unpublished). The C/N ratios of the various soil organic matter pools are derived from the overall C/N ratio of the soil, which is around 15 for a sandy soil and around 10 for a clay soil (Nordmeyer & Richter, 1985). We assume that this difference is the result of a difference in C/N ratio of the stabilized organic matter (SOM), which is therefore set at 10 for a clay soil and at 20 for a sandy soil. Fractionation of organic soil nitrogen shows a decreasing C/N ratio with decreasing particle size (Cameron & Posner, 1979; Amato & Ladd, 1980; Anderson et al., 1981). Assuming that the smallest particles (clay) are associated with protected organic matter (POM), its C/N ratio is set at 10 and the C/N ratio of nonprotected organic matter at 15, for both a sandy and a clay soil.

Simulations are carried out under optimum moisture conditions and a constant temperature of 15 °C.

Table 1a. Standard parameter values for a clay and a sandy soil.

State variables (kg C ha <sup>-1</sup> )	C/N ratio (kg C (kg N) <sup>-1</sup> )	Transformation from → to	Decomposition rate (d <sup>-1</sup> )	Efficiency
C <sub>dpm</sub>	6	DPM → BIOM	k <sub>1</sub> 0.2	E <sub>1</sub> 0.4
C <sub>spm</sub>	150	SPM → BIOM	k <sub>2m</sub> 0.1	E <sub>2</sub> 0.3
C <sub>rpm</sub>	100	RPM → N(P)OM	k <sub>3m</sub> 0.02	E <sub>3</sub> 1.0
C <sub>N</sub>	15	NOM → BIOM	k <sub>5</sub> 0.01	E <sub>5</sub> 0.25
		NOM → SOM	k <sub>8</sub> 1.0E-06	E <sub>8</sub> 1.0
C <sub>p</sub>	10	POM → BIOM	k <sub>6</sub> 0.0003	E <sub>6</sub> 0.2
		POM → SOM	k <sub>9</sub> 1.0E-06	E <sub>9</sub> 1.0
C <sub>S</sub>	10 <sup>a</sup> 20 <sup>b</sup>	SOM → BIOM	k <sub>7</sub> 8.0E-07	E <sub>7</sub> 0.2
C <sub>B</sub>	8	BIOM → NOM	k <sub>4n</sub> 0.5	E <sub>4</sub> 1.0
		BIOM → POM	k <sub>4p</sub> 0.005	E <sub>4</sub> 1.0
Protected biomass as a fraction of total soil organic carbon				
C <sub>B,max</sub> /C <sub>T</sub>			0.018 <sup>a</sup>	0.016 <sup>b</sup>
α <sub>p</sub> , fraction of decomposing microbial biomass into protected organic matter			0.7 <sup>a</sup>	0.3 <sup>b</sup>

Table 1b. Initial conditions for a clay and a sandy soil.

Initial conditions <sup>c</sup>	Clay	Sand
Total soil organic carbon C <sub>T</sub> (kg ha <sup>-1</sup> )	54000	31000
Fraction NOM, C <sub>N</sub> /C <sub>T</sub>	0.007	0.023
Fraction POM, C <sub>p</sub> /C <sub>T</sub>	0.43	0.41
Fraction SOM, C <sub>s</sub> /C <sub>T</sub>	0.55	0.55
Fraction BIOM, C <sub>B</sub> /C <sub>T</sub>	0.018	0.016

<sup>a</sup> Clay soil.

<sup>b</sup> Sandy soil.

<sup>c</sup> The initial conditions are steady state outputs of the model simulated with the k<sub>i</sub> and E<sub>i</sub> values given in Table 1a, a carbon input (C<sub>inp</sub>) of 10 kg ha<sup>-1</sup> d<sup>-1</sup> with a C/N ratio of 25, at a temperature of 15 °C.

**Model behaviour**

*Steady state solutions in a constant environment*

In a steady state the total flux into each state variable equals the total flux out of that state variable. In the steady state of this model, carbon input by residues is in balance with carbon output by respiration, and nitrogen input by residues is in balance with nitrogen output by net mineralization.

Although steady state conditions are never reached in practical agriculture nor in field experiments, in a model it usually provides the best means of exploring and understanding a complex system. For models with a single steady state condition (such as the present model under the applied conditions), the steady state values are independent of the initial conditions.

Analytically, the steady state values for the state variables follow from Equations (11) – (17) by setting the left-hand side to zero, and solving the equations for the seven variables:

$$C_{dpm} = \frac{F_{dpm} \times C_{inp}}{k_1} \tag{18}$$

$$C_{spm} = \frac{F_{spm} \times C_{inp}}{k_2} \tag{19}$$

$$C_{rpm} = \frac{F_{rpm} \times C_{inp}}{k_3} \tag{20}$$

$$C_B - C_{B,max} = [ - E_1 \times F_{dpm} \times C_{inp} - E_2 \times F_{spm} \times C_{inp} + k_{4p} \times C_{B,max} - \tag{21}$$

$$\frac{(0.5 \times E_3 \times F_{rpm} \times C_{inp}) + (1 - \alpha_p) \times E_4 \times k_{4p} \times C_{B,max} \times (E_5 \times k_5 + E_7 \times E_8 \times k_8)}{k_5 + k_8}$$

$$- \frac{(0.5 \times E_3 \times F_{rpm} \times C_{inp}) + \alpha_p \times E_4 \times k_{4p} \times C_{B,max} \times (E_6 \times k_6 + E_7 \times E_9 \times k_9)}{k_6 + k_9} ] /$$

$$[ - k_{4n} + \frac{(1 - \alpha_p) \times E_4 \times k_{4n} \times (E_5 \times k_5 + E_7 \times E_8 \times k_8)}{k_5 + k_8} +$$

$$\frac{\alpha_p \times E_4 \times k_{4n} \times (E_6 \times k_6 + E_7 \times E_9 \times k_9)}{k_6 + k_9} ]$$

$$C_N = \frac{0.5 \times E_3 \times F_{rpm} \times C_{inp} + (1 - \alpha_p) \times E_4 \times (k_{4p} \times C_{B,max} + k_{4n} \times (C_B - C_{B,max}))}{k_5 + k_8} \tag{22}$$

$$C_p = \frac{0.5 \times E_3 \times F_{rpm} \times C_{inp} + \alpha_p \times E_4 \times (k_{4p} \times C_{B,max} + k_{4n} \times (C_B - C_{B,max}))}{k_6 + k_9} \quad (23)$$

$$C_s = \frac{E_8 \times k_8 \times C_N + E_9 \times k_9 \times C_p}{k_7} \quad (24)$$

$$C_T = C_N + C_p + C_s + C_B \quad (25)$$

Without input, no steady state can be reached. Symbols are explained in Tables 1a and 1b. The predicted steady state of the model simulated with the  $k_i$  and  $E_i$  values of Table 1a, a carbon input ( $C_{inp}$ ) of 10 kg C ha<sup>-1</sup>d<sup>-1</sup> with a C/N ratio of 25 ( $F_{dpm} = 0.20$ ,  $F_{spm} = 0.65$ ,  $F_{rpm} = 0.15$ ) is shown in Table 1b. The total amount of soil organic carbon ( $C_T$ ) in a clay soil is almost twice as high as in a sandy soil; the fraction NOM is about three times higher in a sandy soil, the fraction POM and microbial biomass is lower in a sandy soil, whereas the fraction SOM is equal in

Table 2. Steady state conditions for a clay and a sandy soil with different amounts of daily carbon input ( $C_{inp}$ ) and different types of residue ((C/N)<sub>inp</sub>). Symbols are explained in Tables 1a and 1b. MIN-net is net mineralization.

$C_{inp}$ (kg C ha <sup>-1</sup> d <sup>-1</sup> )	(C/N) <sub>inp</sub> <sup>a</sup>	$C_{dpm}$	$C_{spm}$	$C_{rpm}$	$C_T$ (kg C ha <sup>-1</sup> )	$C_B/C_T$	$C_N/C_T$ (fraction of $C_T$ )	$C_p/C_T$	$C_s/C_T$	MIN-net (kg N ha <sup>-1</sup> d <sup>-1</sup> )
<i>Clay</i>										
10	20	30	184	153	52200	0.018	0.007	0.43	0.55	0.55
	25	20	278	263	54220	0.018	0.007	0.43	0.55	0.39
	40	10	273	390	56240	0.018	0.008	0.43	0.55	0.13
	65	5	308	550	59000	0.018	0.008	0.43	0.55	0.16
5	25	10	114	132	27120	0.018	0.007	0.43	0.55	0.20
	40	5	136	195	28120	0.018	0.008	0.43	0.55	0.12
2	40	2	55	78	11250	0.018	0.008	0.43	0.55	0.05
<i>Sand</i>										
10	20	30	184	153	28400	0.016	0.024	0.41	0.55	0.55
	25	20	278	263	31400	0.016	0.023	0.41	0.55	0.39
	40	10	273	390	34470	0.016	0.021	0.42	0.55	0.13
	65	5	308	550	37820	0.016	0.020	0.42	0.55	0.16
5	25	10	114	132	15720	0.016	0.023	0.41	0.55	0.20
	40	5	136	195	17230	0.016	0.021	0.42	0.55	0.12
2	40	2	55	78	6900	0.016	0.021	0.42	0.55	0.05

<sup>a</sup> C/N ratio 20:  $F_{dpm} = 0.30$ ,  $F_{spm} = 0.60$ ,  $F_{rpm} = 0.10$

C/N ratio 25:  $F_{dpm} = 0.20$ ,  $F_{spm} = 0.65$ ,  $F_{rpm} = 0.15$

C/N ratio 40:  $F_{dpm} = 0.10$ ,  $F_{spm} = 0.70$ ,  $F_{rpm} = 0.20$

C/N ratio 65:  $F_{dpm} = 0.05$ ,  $F_{spm} = 0.70$ ,  $F_{rpm} = 0.25$

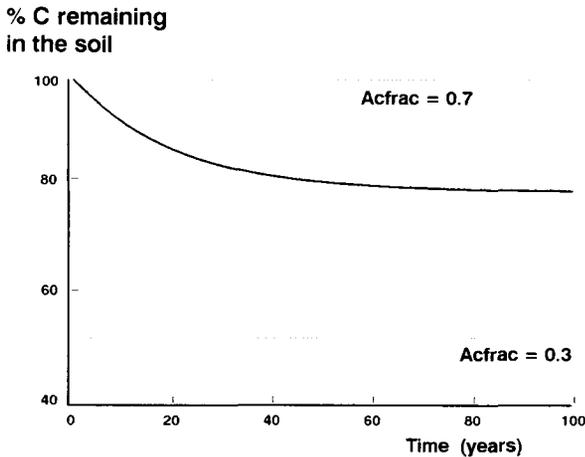


Fig. 2 Effect of changing the parameter  $\alpha_p$  from 0.7 to 0.3 (solid line) on the total C content of a soil (with a constant input of  $10 \text{ kg C ha}^{-1} \text{ d}^{-1}$ ). The upper dotted line shows the steady state situation of a clay soil ( $\alpha_p$  is 0.7) and the lower dotted line that of a sandy soil ( $\alpha_p$  is 0.3).

both soils. The steady state value of the fraction BIOM is the maximum capacity of the soil to protect microorganisms.

Table 2 shows steady state conditions for a clay and a sandy soil for different amounts of daily carbon input and different types of residues. A lower input results in a lower total amount of soil organic carbon ( $C_T$ ) and a lower net mineralization (MIN-net). The absolute value of all state variables decreases with a lower input, without affecting their distribution. Application of residues with a high fraction of lignin leads to a slightly higher level of soil organic carbon. Daily net mineralization is higher with higher proportions of DPM.

The effect of  $\alpha_p$ , governing the distribution of carbon from decomposing microbial biomass between the protected and nonprotected soil organic matter, on total soil organic carbon is shown in Figure 2. Lowering the value  $\alpha_p$  from 0.7 to 0.3 results in a decrease in total soil organic carbon because the nonprotected soil organic matter has a rapid turnover. In the new steady state situation the fraction of protected soil organic matter is smaller and the fraction of nonprotected soil organic matter larger. The steady state value of the fraction of stabilized soil organic matter is independent of  $\alpha_p$ . The new equilibrium situation for the active soil organic matter is reached in approximately 100 years. It will take more than 1000 years to reach the final steady state, due to the much longer time constant of the stabilized soil organic matter.

#### *Transient solutions in a constant environment*

To examine the influence of soil type on nitrogen mineralization and immobilization, simulation runs were carried out in a constant environment. In the model, a sandy and clay soil only differ in  $\alpha_p$  (Fig. 2). Figure 3a shows cumulative net

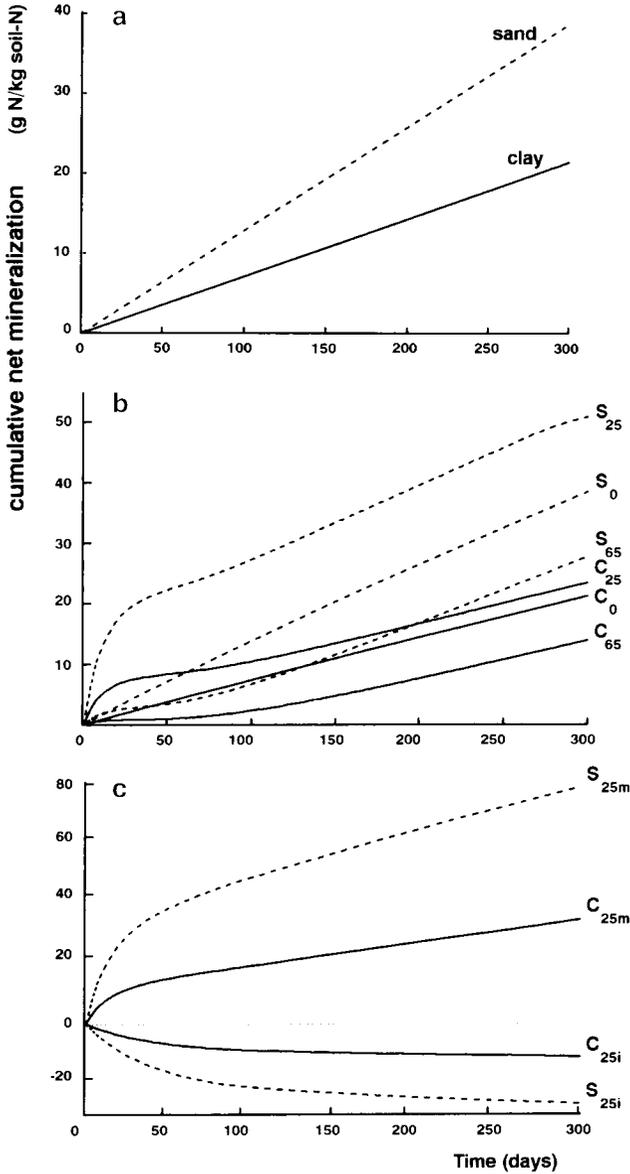


Fig. 3 (a) Cumulative net mineralization for a period of 300 days in a sandy (dotted line) and a clay soil (solid line) without residue input. (b) Cumulative net mineralization in clay soils and sandy soils for a period of 300 days without input or with an input of 2000 kg C ha<sup>-1</sup> and a C/N ratio of 25 or 65. C<sub>0</sub>: clay soil, no input; S<sub>0</sub>: sandy soil, no input; C<sub>25</sub>: clay soil, C/N = 25 ( $F_{dpm} = 0.20$ ,  $F_{spm} = 0.65$ ,  $F_{rpm} = 0.15$ ); S<sub>25</sub>: sandy soil, C/N = 25 ( $F_{dpm} = 0.20$ ,  $F_{spm} = 0.65$ ,  $F_{rpm} = 0.15$ ); C<sub>65</sub>: clay soil, C/N = 65 ( $F_{dpm} = 0.05$ ,  $F_{spm} = 0.70$ ,  $F_{rpm} = 0.25$ ); S<sub>65</sub>: sandy soil, C/N = 65 ( $F_{dpm} = 0.05$ ,  $F_{spm} = 0.70$ ,  $F_{rpm} = 0.25$ ). (c) Cumulative mineralization and immobilization in a clay and a sandy soil for a period of 300 days both with an input of 2000 kg C ha<sup>-1</sup> and a C/N ratio of 25 for a period of 300 days. C<sub>25m</sub>: cumulative mineralization clay soil; C<sub>25i</sub>: cumulative immobilization clay soil; S<sub>25m</sub>: cumulative mineralization sandy soil; S<sub>25i</sub>: cumulative immobilization sandy soil.

mineralization in a clay and a sandy soil without residue input, illustrating the higher rate in the sandy soil.

The effect of the quality of residues (C/N ratio 25 or 65) on cumulative net mineralization in clay and sandy soils is illustrated in Figure 3b. Decomposition of residues with a C/N ratio of 25 results in higher net mineralization whereas decomposition of residues with a C/N ratio of 65 results in lower net mineralization compared with the situation without residue input. The release of nitrogen in both situations is higher in sandy soils. For the situation with a C/N ratio of 25, the contribution of mineralization and immobilization are analysed in Figure 3c. Mineralization ( $S_{25m}$ ,  $C_{25m}$ ) is mainly the result of decomposition of easily decomposable material (DPM) which after 30 days is practically completed; the slow increase after that, originates from native soil organic matter. The rate of nitrogen release due to decomposition of DPM is higher in the sandy soil than in the clay soil. Decomposition of structural and resistant material leads to immobilization (Fig. 3c,  $S_{25i}$  and  $C_{25i}$ ), which is also higher in the sandy soil than in the clay soil. After complete decomposition of the residues the net mineralization curves run parallel to the curves referring to the situation without residue input ( $S_0$  and  $C_0$ ).

## Discussion

The model for soil organic matter dynamics presented in this paper differs from the models of van Veen (van Veen & Paul, 1981; van Veen et al., 1984; van Veen et al., 1985) in several ways:

- only active soil organic matter is subdivided into a protected and nonprotected component,
- the nonprotected organic matter component is not subdivided into a recalcitrant and a decomposable component,
- the maximum capacity to protect microorganisms is dependent on total soil organic carbon,
- lignin compounds in residues are partitioned between nonprotected and protected organic matter,
- the proportion of lignin in residues affects accessibility and thus the rate of decomposition of structural material,
- lignin is released as microbes decompose (hemi)cellulose.

The models of van Veen were intended to describe long-term effects of cultivation and/or erosion, effects of drying and rewetting of soils, and to simulate field situations. In this study the aim is to simulate soil organic matter dynamics as a first step toward simulating the effects of soil type on nitrogen mineralization. Hence, no attempt has been made to calibrate or validate the model on the basis of field or incubation experiments; the model is descriptive rather than explanatory.

Some steady state results of Table 2 are comparable with field situations. A residue input of 10 kg C ha<sup>-1</sup> d<sup>-1</sup> with a C/N ratio of 25 corresponds with the input in temperate grassland (van Veen & Paul, 1981; Swift et al., 1979), a residue input of 5 kg C ha<sup>-1</sup> d<sup>-1</sup> with a C/N ratio of 40 corresponds with inputs on arable land (e.g. wheat), and a residue input of 10 kg C ha<sup>-1</sup> d<sup>-1</sup> with a C/N ratio of 65

Table 3. Steady state results of total soil organic carbon, organic matter content and accumulated (undecomposed) surface litter ( $C_{dpm} + C_{spm} + C_{rpm}$ ) simulated with different amounts of input ( $C_{inp}$ ) and different C/N ratios of the input ( $(C/N)_{inp}$ ), for a clay and a sandy soil. The organic matter content is calculated assuming a carbon content of 58 %, a soil bulk density of 1000 (clay soil) and 1300 kg m<sup>-3</sup> (sandy soil), and a rooting depth of 10 cm.

$C_{inp}$ (kg C ha <sup>-1</sup> d <sup>-1</sup> )	$(C/N)_{inp}$	Soil use	Soil organic carbon (kg C ha <sup>-1</sup> )	Organic matter (%)	$C_{dpm} + C_{spm} + C_{rpm}$ (kg C ha <sup>-1</sup> )
10	25	grassland (clay)	54220	9.3	511
		grassland (sand)	31400	4.2	511
5	40	arable (clay)	28120	4.8	336
		arable (sand)	17230	2.3	336
10	65	forest (clay)	59000	10.2	863
		forest (sand)	37820	5.0	863

corresponds with a temperate forest (Swift et al., 1979; Staaf & Berg, 1980). Table 3 shows the simulated steady states in terms of total soil organic carbon, soil organic matter content and amounts of accumulated surface litter ( $C_{DPM} + C_{SPM} + C_{RPM}$ ) of these various agricultural systems. Organic matter content of a clay soil is higher than of a sandy soil, and is higher under grassland and forest than under arable cropping. Kortleven (1963) already reported that the soil organic matter content under grassland is, on average, two to five times higher than under arable cropping and it increases with clay and silt content of the soil. The results of the steady state simulations indicate that returning residues to soils helps to maintain soil organic matter content and soil fertility in terms of nitrogen mineralization.

It has often been observed that decomposition of residues and nitrogen mineralization is slower in soils with heavier texture (Jenkinson, 1977; van Veen et al., 1985), and mineralization of native soil organic nitrogen is also slower in clay than in sandy soils (Hassink, unpublished). The pattern of nitrogen mineralization of different residues in different soils is similar, as illustrated in Figures 3a en 3b. During the first 15 days, a rapid increase in mineral nitrogen is calculated in both soils when residues with a low C/N ratio are decomposed, due to the removal (outwash) of soluble components like carbohydrates and proteins and microbial decomposition of simple organic compounds (Swift, 1985). After 20 days, the release of nitrogen decreases during decomposition of structural and resistant material, both with a low nitrogen content. The net mineralization of nitrogen from similar residues is higher in the sandy soil than in the clay soil. This is due to the higher fraction of non-protected organic matter with a relatively high turnover rate. This is illustrated in Table 4, showing the relative contribution of the various fractions to nitrogen mineralization for both soil types for a period of 300 days, and the percentage nitrogen in those various soil organic matter pools. Although the nonprotected organic nitrogen is a very small fraction of total soil nitrogen, its contribution to mineralization is considerable, especially in the sandy soil. Without input, protected soil or-

MODELLING SOIL ORGANIC MATTER DYNAMICS

Table 4. Nitrogen in the various soil organic matter components as a percentage of total soil organic nitrogen, and the relative contribution of the components to nitrogen mineralization for a clay and a sandy soil. Mineralization is calculated with the model for a period of 300 days.

	% of soil N	Relative contribution to mineralization (%)		
		no input	input 2000 kg C ha <sup>-1</sup>	
			C/N = 25 <sup>a</sup>	C/N = 65 <sup>b</sup>
<i>Clay</i>				
BIOM	2.2	18.9	28.0	25.9
NOM	0.5	12.1	14.5	15.1
POM	42.7	68.8	57.4	58.9
SOM	54.6	0.2	0.1	0.1
<i>Sand</i>				
BIOM	2.8	20.5	36.3	34.0
NOM	2.1	28.7	29.5	30.1
POM	56.9	50.6	34.2	35.8
SOM	38.2	0.2	0	0.1

<sup>a</sup> C/N ratio 25 ( $F_{dpm} = 0.20$ ,  $F_{spm} = 0.65$ ,  $F_{rpm} = 0.15$ )

<sup>b</sup> C/N ratio 65 ( $F_{dpm} = 0.05$ ,  $F_{spm} = 0.70$ ,  $F_{rpm} = 0.25$ )

ganic matter (POM) provides the largest contribution to mineralization in both soils while stabilized soil organic matter (SOM) hardly contributes. Input of residues increases microbial biomass and, as a result, its contribution to mineralization. The simulated values of Table 4 agree with the results of a study by Paul & Juma (1981), who measured the contribution of the various soil fractions to nitrogen mineralization in a loam soil. They found that the contribution of the microbial biomass was 28 %, of the active pool 32 %, of the stabilized pool 40 % and of the old pool 0 %, close to the results presented in Table 4 for the sandy soil.

To analyse decomposition of native soil organic matter and added organic materials, and to analyse and explain differences between soils in terms of nitrogen mineralization and mineralization patterns, in mathematical models it is necessary to differentiate between specific components of native soil organic matter and residues (van Veen, 1987). Components of residues have mostly been determined by chemical methods (Goering & van Soest, 1970); these are widely used and accepted. Less consistency exists on methods to fractionate native soil organic matter (van Veen, 1987). Hydrolysis of soil organic matter distinguishes old and young fractions, as shown by radiocarbon dating (Martel & Paul, 1974; Paul & van Veen, 1978). However, it is doubtful whether chemical fractionation techniques alone are sufficient to estimate the size of biologically important fractions. It is evident that the availability of organic materials as a substrate for microorganisms is not only determined by their chemical composition, but also by their spatial distribution in the soil. Observed differences in accessibility of active organic matter to biological transforma-

tion lead to a further subdivision: an active, physically protected component and an active nonprotected component (Jenkinson & Rayner, 1977; van Veen & Paul, 1981; van Veen et al., 1985). Soils with a high clay and/or silt content have a high fraction of protected soil organic matter, which leads to higher total soil organic matter contents and lower net mineralization. Assuming that in a clay soil a higher proportion of the decomposing microbial biomass is retained near protected organic matter, a larger fraction moves into the protected organic matter and a smaller fraction into nonprotected organic matter, compared with a sandy soil.

The mechanism involved in protection is not yet clear. It could be adsorption at the surface of the clay minerals or location within and between soil aggregates at sites inaccessible to microorganisms. This would suggest that not only soil texture influences rate of decomposition, but also soil structure. By breaking soil structure and/or mixing the soil, e.g. under cultivation, inaccessible organic matter may become available to microorganisms. In the model the effect of cultivation can be simulated by lowering  $\alpha_p$ , the proportion from decomposing microbial biomass transformed into protected soil organic matter, or by increasing the nonprotected active organic matter component (and decreasing the protected organic matter component), or a combination of the two. Figure 4 shows the effects of both changes in terms of cumulative net mineralization in both soil types. Reducing  $\alpha_p$  in a sandy soil from 0.3 to 0.1 increased cumulative net mineralization; on a clay soil a reduction of  $\alpha_p$  from 0.7 to 0.3 resulted in a stronger increase in mineralization. In

**cumulative  
net mineralization**  
(g N/kg soil-N)

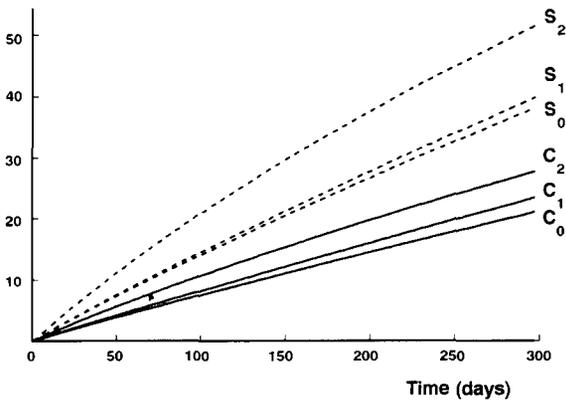


Fig. 4 Cumulative net mineralization in a clay and a sandy soil with different values of  $\alpha_p$  and different fractions active soil organic matter.

S<sub>0</sub>: sandy soil,  $\alpha_p = 0.3$ , fraction NOM = 0.023, fraction POM = 0.41; S<sub>1</sub>: sandy soil,  $\alpha_p = 0.1$ , fraction NOM = 0.023, fraction POM = 0.41; S<sub>2</sub>: sandy soil,  $\alpha_p = 0.3$ , fraction NOM = 0.05, fraction POM = 0.383; C<sub>0</sub>: clay soil,  $\alpha_p = 0.7$ , fraction NOM = 0.007, fraction POM = 0.43; C<sub>1</sub>: clay soil,  $\alpha_p = 0.3$ , fraction NOM = 0.007, fraction POM = 0.43; C<sub>2</sub>: clay soil,  $\alpha_p = 0.7$ , fraction NOM = 0.03, fraction POM = 0.401.

both soils, increasing the fraction of nonprotected active organic matter has a more pronounced effect on total net mineralization than reducing  $\alpha_p$ . Other effects of cultivation could be a change in environmental conditions such as higher oxygen contents which induces higher rates of decomposition and thus higher mineralization rates. In simulating the effect of cultivation (ploughing, tillage) on nitrogen mineralization, one has to take all these factors into account.

So far, the parameter  $\alpha_p$  describing the partitioning between nonprotected and protected active organic matter was used as a key parameter to characterize the effect of soil type on decomposition. In further model development, the significance of  $\alpha_p$  could increase if the effect of other soil characteristics, like structure, porosity, surface properties and aggregation, can be incorporated. Pore size distribution could give an indication of the accessibility of substrates to decomposition by microorganisms. Pore size distribution is a function of soil texture and soil structure (Papendick & Campbell, 1981); generally, fine-textured clay soils have a larger proportion of small pores. Changing soil structure, e.g. by cultivation, may change pore size and pore size distribution.

In developing the model, it was attempted to increase insight in soil organic matter dynamics of different soils. Organic matter is undoubtedly stabilized by physical protection, which may differ substantially between soils of different texture. Different organic matter components were distinguished which at this stage constitutes a working hypothesis, which, however, was not put to a rigorous test by comparison with field data. In further development of the model particular attention will be paid to the effects of soil structure and soil texture and to the spatial distribution of organic materials and their decomposers.

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## Ammonia volatilization from arable land after application of cattle slurry. 2. Derivation of a transfer model

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### Abstract

Ammonia, volatilized from animal manures after land-spreading, is one of the major sources of acid deposition in the Netherlands. A model for transfer of ammonia from arable land to the atmosphere after surface application or incorporation of cattle slurry is presented. The model can be used to study the interactions of the chemical, physical and environmental factors influencing volatilization losses and their combined influence on  $\text{NH}_3$  volatilization under field conditions. The model employs the following flux equation:  $R = k (C_s - C_a)$  where  $k$  is a transfer function,  $C_s$  is the  $\text{NH}_{3(g)}$  surface concentration and  $C_a$  is the atmospheric  $\text{NH}_{3(g)}$  background concentration. The rate of volatilization  $R$  can be calculated at any moment after application, provided  $k$ ,  $C_s$  and  $C_a$  are known at this moment. The model therefore basically consists of modules which yield these variables.

*Keywords:* ammonia volatilization, transfer model, cattle slurry, arable land, surface application, incorporation

### Introduction

Annual ammonia ( $\text{NH}_3$ ) emissions from liquid animal manures in the Netherlands are estimated to be  $2.5 \times 10^5$  Mg. A substantial part of the  $\text{NH}_3$  is deposited on nearby sites, and contributes to soil acidification upon transformation into  $\text{HNO}_3$  through nitrification. It is estimated that volatilization of  $\text{NH}_3$  after land-application of cattle slurry constitutes 30 % of the total emission.

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Results of field experiments on  $\text{NH}_3$  volatilization after application of cattle slurry to arable land have been reported by Beauchamp et al. (1982) and van der Molen et al. (1989; 1990). As the interactions involved in the  $\text{NH}_3$ -volatilization process are very complex, modelling the process has become a prerequisite for understanding the dynamics of the process, and for interpretation of the results of experiments. As far as we know there are no models available describing the process of  $\text{NH}_3$  volatilization under field conditions from arable land after application of cattle slurry.

In this paper, we present a transfer model for  $\text{NH}_3$  volatilization from arable land after surface application or incorporation of cattle slurry. The model can be used to study the interaction of the chemical, physical and environmental factors influencing volatilization losses and their combined influence on  $\text{NH}_3$  volatilization under field conditions. The work is part of an integrated programme which deals with the chemical, physical and biological aspects of the application of animal manures to soils. The model presented in this paper serves as the base for a predictive  $\text{NH}_3$  volatilization model.

## Model description

### General theory

Cattle slurry is a mixture of urine and faeces excreted by cattle. Before application to the land, the slurry is kept in storage tanks. During storage, urea, which is a component of urine, undergoes hydrolysis catalysed by urease according to:



It is because of this process that cattle slurry from storage tanks contains ammoniacal N, which may be lost through  $\text{NH}_3$  volatilization after application to the land. The amount of ammoniacal N that may volatilize after application strongly depends on the amount being lost while the animals are housed, and during storage and application of the liquid manure.

Volatilization of  $\text{NH}_3$  after land-application will take place if the  $\text{NH}_{3(\text{g})}$  concentration at the surface exceeds the  $\text{NH}_{3(\text{g})}$  concentration in the air. When the ammonia profile in the air is in equilibrium with the concentration at the surface, the rate of volatilization  $R(t)$  ( $\mu\text{g N m}^{-2} \text{s}^{-1}$ ) can be expressed as the difference between the  $\text{NH}_{3(\text{g})}$  surface concentration  $C_s(t)$  ( $\mu\text{g N m}^{-3}$ ) and the concentration  $C_a(t)$  ( $\mu\text{g N m}^{-3}$ ) at a specified height  $z_a$  (m) above the surface (Rachhpal-Singh & Nye, 1986):

$$R(t) = k(t)\{C_s(t) - C_a(t)\} \quad (2)$$

where  $k(t)$  ( $\text{m s}^{-1}$ ) is a transfer function. The rate of volatilization  $R(t)$  as described by Equation 2 can be calculated at any moment after application when all three terms on the right-hand side of Equation 2 are known at these very moments. The model basically consists of two main modules, which yield  $k(t)$  and

$C_s(t)$ , respectively. The atmospheric  $\text{NH}_{3(g)}$  concentration,  $C_a(t)$ , is required as input for the model.

The transfer module describes the volatilization process itself, i.e. the transfer of  $\text{NH}_{3(g)}$  from the earth's surface into the atmosphere, and yields the transfer function  $k(t)$ . The description of the transfer function is obtained from the same theory which has been developed for evaporation of water into the atmosphere, but which is sufficiently general to allow description of volatilization of  $\text{NH}_3$  as well.

In the soil module the magnitude of the  $\text{NH}_{3(g)}$  concentration at the surface,  $C_s(t)$ , is calculated. In order to determine this concentration, a number of chemical and physical processes which define the distribution of ammoniacal N over the different phases of the soil/manure system and the transport within the system, have to be taken into account. In addition to  $\text{NH}_3$  volatilization, other processes may influence the ammoniacal-N content of the system during a volatilization event. These are biological processes which consume (nitrification, immobilization) or produce (mineralization) ammoniacal N. A more accurate description of the two modules mentioned so far is given below.

### *Soil module*

The distribution of the ammoniacal N, applied with slurry, immediately after application depends on the method of application. In case of surface application, slurry is spread on the land after which the slurry infiltrates into the soil, whereas in case of incorporation the slurry is mixed through the upper layer of soil after spreading. For both surface application and incorporation, the initial distribution of the ammoniacal N is assumed to be uniform down to a certain depth. The difference between the two application techniques appears in the depth over which the ammoniacal N is initially distributed. This depth,  $L_{\text{init}}$  (m), is selected to reflect the principal extent of cattle slurry placement, i.e. in case of surface application the effective distance over which infiltration occurs, and in case of incorporation the thickness of the soil layer which the slurry is mixed through. The assumption of a uniform initial ammoniacal-N distribution with depth down to depth  $L_{\text{init}}$  implies that, in case of surface application, infiltration of slurry takes place instantaneously.

For the purpose of modelling, the ammoniacal-N content at the soil surface is assumed to be uniform to some fixed depth,  $L_1$  (m). Thus, throughout a top compartment the temporal variations in ammoniacal-N content resulting from volatilization and chemical, physical or biological processes in the soil are assumed to be uniform. Below this depth, a second compartment of variable thickness  $L_2(t)$  (m) is assumed from which no volatilization takes place. This compartment acts as a storage reservoir for the amount of ammoniacal N originating from the slurry that is placed below depth  $L_1$ . The front of the ammoniacal-N content profile in the soil coincides with the bottom of this compartment at a depth  $L(t)$  (m), where a step-change in ammoniacal-N content occurs. Within this compartment the distribution of the ammoniacal N present and the temporal variations in ammoniacal-N content due to chemical, physical or biological processes are also assumed to be uniform with depth.

As the initial distribution of the ammoniacal N is assumed to be uniform down to depth  $L_{init}$ , the amounts of ammoniacal N initially stored in the two compartments,  $NH_{x1,i}$  and  $NH_{x2,i}$  (both in  $\mu\text{g N m}^{-2}$ ), are defined by the total amount of ammoniacal N applied with the slurry,  $NH_{x,app}$  ( $\mu\text{g N m}^{-2}$ ), the depth  $L_{init}$  over which this ammoniacal N is placed initially and the thickness  $L_1$  of the top compartment ( $L_1$  is a fixed value for a certain type of application; its magnitude is obtained from calibration of the model). The model therefore requires  $NH_{x,app}$ ,  $L_{init}$  and  $L_1$  as input, and calculates  $NH_{x1,i}$ ,  $NH_{x2,i}$  and the initial value of  $L_2(t)$ ,  $L_{2,i}$ , as follows:

$$L_{2,i} = L_{init} - L_1 \tag{3}$$

$$NH_{x1,i} = NH_{x,app} \times L_1/L_{init} \tag{4a}$$

$$NH_{x2,i} = NH_{x,app} \times L_{2,i}/L_{init} \tag{4b}$$

Figure 1 gives a schematic representation of the distribution of the total amount of ammoniacal N originating from the slurry immediately after application.

The volumetric flux of water,  $J_w(t)$  ( $\text{m s}^{-1}$ ), through the two compartments, which is assumed to be constant with depth, is calculated from the net difference between the evaporation rate,  $E(t)$  ( $\text{m s}^{-1}$ ), and the rainfall rate,  $P(t)$  ( $\text{m s}^{-1}$ ), i.e.:

$$J_w(t) = E(t) - P(t) \tag{5}$$

In order to calculate  $J_w(t)$  throughout a volatilization event from Equation 5, data on evaporation and rainfall rates throughout the event are required as input.

The flux of ammoniacal N between the two compartments is assumed to take place by convective transport in the liquid phase and diffusive transport in both the liquid and the gas phase.

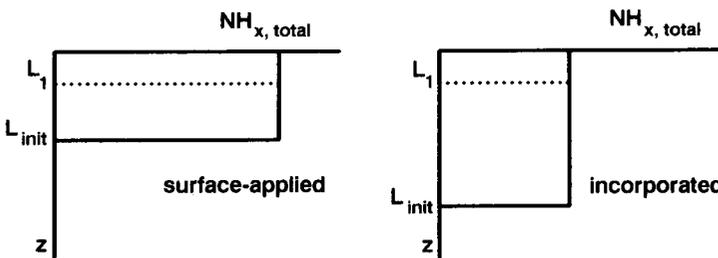


Fig. 1. Schematic representation of the initial distribution of the total amount of ammoniacal N originating from the slurry following surface application and following incorporation of the same amounts of slurry.

Convective transport,  $J_c(t)$  ( $\mu\text{g N m}^{-2} \text{s}^{-1}$ ), is calculated as:

$$J_c(t) = J_w(t) \times ([\text{NH}_3]_{\text{aq}} + [\text{NH}_4^+]_{\text{aq}}) \quad (6)$$

where  $[\text{NH}_3]_{\text{aq}}$  and  $[\text{NH}_4^+]_{\text{aq}}$  are the concentrations ( $\mu\text{g N m}^{-3}$ ) of  $\text{NH}_3$  and  $\text{NH}_4^+$  in solution. Ammoniacal N is transported from the bottom compartment to the top compartment if the net water flux is in the upward direction,  $E(t) > P(t)$ , whereas transport of ammoniacal N from the top compartment to the bottom compartment takes place in case of a downward net water flux,  $E(t) < P(t)$ . The way  $[\text{NH}_3]_{\text{aq}}$  and  $[\text{NH}_4^+]_{\text{aq}}$  are calculated is shown below.

Diffusive transport,  $J_d(t)$  ( $\mu\text{g N m}^{-2} \text{s}^{-1}$ ), is calculated as:

$$J_d(t) = J_{\text{dg}}(t) + J_{\text{daq1}}(t) + J_{\text{daq2}}(t) \quad (7)$$

where subscripts g and aq denote gaseous and aqueous, respectively; the terms on the right-hand side are calculated as:

$$J_{\text{dg}}(t) = - D_g \times ([\text{NH}_3]_{\text{g1}} - [\text{NH}_3]_{\text{g2}}) \times L_d^{-1} \quad (8a)$$

$$J_{\text{daq1}}(t) = - D_{\text{aq}} \times ([\text{NH}_3]_{\text{aq1}} - [\text{NH}_3]_{\text{aq2}}) \times L_d^{-1} \quad (8b)$$

$$J_{\text{daq2}}(t) = - D_{\text{aq}} \times ([\text{NH}_4^+]_{\text{aq1}} - [\text{NH}_4^+]_{\text{aq2}}) \times L_d^{-1} \quad (8c)$$

The subscripts 1 and 2 on the right-hand side refer to the compartment number. The terms  $D_g$  and  $D_{\text{aq}}$  denote the gaseous and aqueous diffusion coefficient, respectively, and are derived below. The diffusion length,  $L_d$ , is calculated as:  $L_d = \{L_1 + L_2(t)\} \times 0.5$ .

As mentioned earlier, the thickness of the top compartment,  $L_1$ , is fixed for a volatilization event, whereas the thickness of the bottom compartment,  $L_2(t)$ , may deviate from its initial value,  $L_{2,i}$ . By definition the bottom compartment at  $t = 0$  contains all ammoniacal N originating from the slurry that is placed below depth  $L_1$ ; it is assumed that the soil initially did not contain ammoniacal N. The lower boundary of this compartment coincides with the front of the ammoniacal-N content profile in the soil at a depth  $L(t)$ , where a step-change in ammoniacal-N content occurs. In order to keep track of the thickness of the bottom compartment,  $L_2(t)$ , the model calculates the rate  $J_s(t)$  ( $\text{m s}^{-1}$ ), at which the ammoniacal-N front moves through the soil for  $t > 0$ :

$$J_s(t) = \frac{J_w(t)}{\theta_v(t)} \left( \frac{1}{1 + R_D} \right) \quad (9)$$

where  $R_D(-)$  is the retardation factor for the transport of  $\text{NH}_4^+$  (Equation 21), and  $\theta_v(t)$  is the volumetric water content (required as input). The model calculates

the thickness of the bottom compartment,  $L_2(t)$ , after each time step according to:

$$L_2(t) = L_2(t') - J_s(t) \times \Delta t \quad (10)$$

where  $\Delta t$  is the current time step (s) and  $L_2(t')$  is the thickness of the bottom compartment prior to the time step.

The amounts of ammoniacal N present in the two compartments,  $NH_{x1}(t)$  and  $NH_{x2}(t)$  (both in  $\mu\text{g N m}^{-2}$ ), for  $t > 0$ , are calculated according to:

$$NH_{x1}(t) = NH_{x1}(t') - S_1 + I - V \quad (11a)$$

$$NH_{x2}(t) = NH_{x2}(t') - S_2 - I \quad (11b)$$

where the prime denotes the amount of ammoniacal N present prior to the time step;  $S$ ,  $I$  and  $V$  ( $\mu\text{g N m}^{-2}$ ) are a sink term representing the net loss due to biological processes, the net inflow of ammoniacal N due to convective and diffusive transport and the amount of ammoniacal N volatilized, respectively. The magnitude of the terms  $V$ ,  $I$  and  $S$  in Equations 11a and 11b is calculated from the current time step,  $\Delta t$ , and the rates at which volatilization (Equation 2), inflow of ammoniacal N (Equations 6 and 7) and net loss of ammoniacal N due to biological processes,  $s(t)$  ( $\mu\text{g N m}^{-2} \text{ s}^{-1}$ ), occur:

$$V = R(t) \times \Delta t \quad (12)$$

$$I = \{J_c(t) + J_d(t)\} \times \Delta t \quad (13)$$

$$S_1 = s_1(t) \times \Delta t, \quad S_2 = s_2(t) \times \Delta t \quad (14)$$

Data on the rate,  $s(t)$ , at which net loss of ammoniacal N from the system due to biological processes takes place are part of the input for the model. The distribution of the rate  $s(t)$  over the compartments is carried out according to:

$$s_1(t) = s(t) \frac{NH_{x1}(t)}{NH_{x1}(t) + NH_{x2}(t)} \quad (15)$$

$$s_2(t) = s(t) \frac{NH_{x2}(t)}{NH_{x1}(t) + NH_{x2}(t)} \quad (16)$$

The distribution of the amounts of ammoniacal N present in each compartment over the different phases in the soils is calculated from the amount of ammoniacal N present in each compartment,  $NH_{x1}(t)$  and  $NH_{x2}(t)$ , and relationships between the concentrations of the different ammoniacal species.  $NH_{x1}(t)$  and  $NH_{x2}(t)$  can be expressed in terms of the concentrations of the different ammoniacal species as follows:

$$NH_{x1}(t) = L_1 (\theta_g [NH_3]_{g,1} + \theta_v [NH_3]_{aq,1} + \theta_v [NH_4^+]_{aq,1} + \rho_b [NH_4^+]_{s,1}) \quad (17)$$

$$NH_{x2}(t) = L_2(t) (\theta_g [NH_3]_{g,2} + \theta_v [NH_3]_{aq,2} + \theta_v [NH_4^+]_{aq,2} + \rho_b [NH_4^+]_{s,2}) \quad (18)$$

where the subscripts g, aq and s denote concentrations in the soil gaseous phase ( $\mu\text{g N m}^{-3}$ ), the soil aqueous phase ( $\mu\text{g N m}^{-3}$ ) and the soil solid phase ( $\mu\text{g N per kg}$  of dry soil material) respectively;  $\rho_b$  is the dry bulk density of the soil ( $\text{kg m}^{-3}$ ) and  $\theta_g$  is the gas-filled pore volume (-), which is calculated from the porosity,  $\phi$  (-), and the volumetric water content  $\theta_v$  according to:

$$\theta_g = \phi - \theta_v \quad (19)$$

Both  $\phi$  and  $\rho_b$  are required as input for the model.

With  $NH_{x1}(t)$  and  $NH_{x2}(t)$  known from Equations 11a and 11b,  $L_1$  obtained from calibration of the model,  $L_2(t)$  and  $\theta_g$  defined by Equations 10 and 19 and  $\theta_v$  and  $\rho_b$  given with the input, the concentrations on the right-hand sides of Equations 17 and 18 are calculated with the help of the following relationships between the concentrations of the different ammoniacal species.

The partitioning of  $NH_4^+$  between the soil solid and the soil aqueous phases is optionally described by a linear isotherm (Equation 20a), a Freundlich isotherm (Equation 20b), or a Langmuir isotherm (Equation 20c):

$$[NH_4^+]_s = a [NH_4^+]_{aq} \quad (20a)$$

$$[NH_4^+]_s = a ([NH_4^+]_{aq})^b \quad (20b)$$

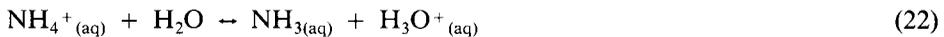
$$[NH_4^+]_s = \frac{a b [NH_4^+]_{aq}}{1 + b [NH_4^+]_{aq}} \quad (20c)$$

where  $[NH_4^+]_{aq}$  and  $[NH_4^+]_s$  are again given in ( $\mu\text{g N m}^{-3}$ ) and ( $\mu\text{g N per kg}$  of dry soil material) respectively;  $a$  and  $b$  are constants, which are input parameters for the model.

The retardation factor  $R_D$  (Equation 9), which is defined as the ratio between the amount of  $NH_4^+$  adsorbed by the soil solid phase and the amount of  $NH_4^+$  in solution (Bolt, 1976), is calculated from:

$$R_D = \frac{\rho_b [NH_4^+]_s}{\theta_v [NH_4^+]_{aq}} \quad (21)$$

The relation between  $NH_4^+$  and  $NH_3$  in solution is calculated from the equilibrium constant  $K_a$  ( $\text{mol l}^{-1}$ ) for the dissociation of  $NH_4^+$  (aq):



$$\frac{[NH_3]_{aq}}{[NH_4^+]_{aq}} = \frac{K_a}{[H_3O^+]_{aq}} \quad (23)$$

where  $K_a$  is calculated from (Hales & Drewes, 1979):

$$\log K_a = - 0.09018 - 2729.92T^{-1} \quad (24)$$

and:

$$[\text{H}_3\text{O}^+]_{\text{aq}} = 10^{-\text{pH}} \quad (25)$$

where  $[\text{H}_3\text{O}^+]_{\text{aq}}$  is expressed in ( $\text{mol l}^{-1}$ ). In order to calculate  $K_a$  and  $[\text{H}_3\text{O}^+]_{\text{aq}}$  from Equations 24 and 25, data on soil temperature (K) and pH are required as input.

The ratio between  $\text{NH}_3$  in the soil solution and the soil gaseous phase is calculated from Henry's law:

$$K_h = [\text{NH}_3]_{\text{aq}}/[\text{NH}_3]_{\text{g}} \quad (26)$$

where Henry's law equilibrium constant (–) is given by (Hales & Drewes, 1979):

$$\log K_h = - 1.69 + 1477.7T^{-1} \quad (27)$$

in which  $T$  is again the absolute soil temperature (K).

Now when all the concentrations on the right-hand-sides of Equations 17 and 18 are known, the description of the soil module has been completed. From the definition of the top compartment, i.e. a uniform ammoniacal-N content distribution from the soil surface down to  $L_1$ , and the use of constant  $\theta_g$ ,  $\theta_v$  and  $\rho_b$  from the soil surface down to  $L(t)$  during a volatilization event, it follows that  $[\text{NH}_3]_{\text{g}}$  equals  $C_s(t)$  (Equation 2). With  $C_s(t)$  known from the soil module and  $C_a(t)$  given as input, only the transfer function  $k(t)$  has to be defined to complete Equation 2 for operation.

### *Transfer module*

As mentioned earlier, volatilization of  $\text{NH}_3$  after land-application will take place if the  $\text{NH}_{3(\text{g})}$  concentration at the surface exceeds the  $\text{NH}_{3(\text{g})}$  concentration in the air. When the ammonia profile in the air is in equilibrium with the concentration at the surface, the rate of volatilization  $R(t)$  can be expressed as the difference between the  $\text{NH}_{3(\text{g})}$  surface concentration  $C_s(t)$  and the concentration  $C_a(t)$  at a specified height  $z_a$  above the surface as described by Equation 2:

$$R(t) = k(t) \{C_s(t) - C_a(t)\} \quad (2)$$

where  $k(t)$  is a transfer function, which is defined by:

$$k(t) = \frac{1}{r_a(x,t) + r_b(t) + r_s(t)} \quad (28)$$

where  $r_a(x,t)$ ,  $r_b(t)$  and  $r_s(t)$  (all in  $s\ m^{-1}$ ) are the aerodynamic resistance between height  $z_a$  and the surface, the resistance of the interfacial sublayer and the surface resistance respectively. The aerodynamic resistance represents the resistance of the turbulent layer between height  $z_a$  (e.g. observation height) and  $z = z_0$ , where  $z_0$  is the aerodynamic roughness length of the surface (m). The roughness length  $z_0$  ranges from 1 mm for smooth bare soil to 1 m for a surface with tall vegetation (e.g. trees; see Wieringa, 1986, for the relation between  $z_0$  and terrain characteristics). The resistance of the interfacial sublayer represents the additional resistance for passive contaminants due to molecular diffusion, which is not present in the case of momentum transfer (e.g. Brutsaert, 1982). The surface resistance represents the resistance of the surface itself and is the result of the diffusion processes from inside the soil/slurry layer towards the air.

In the case of a manured field of limited size, the surface emission is not in equilibrium with the concentration profile and advection plays a dominant role. As schematically shown in Figure 2 an internal boundary layer develops over the manured field. The internal boundary layer depth is a measure for the height over which the volatilization of the manured field is felt.

To model the volatilization rate  $R(t)$  of the manured field we want to relate the difference between the surface concentration  $C_s(t)$  and the background concentration  $C_a(t)$  of the air advected from upstream. This means that we have to estimate the resistance introduced in Equation 28. This is an inhomogeneous diffusion problem with a sudden downstream transition in the surface concentration. The wind forcing remains unchanged because the aerodynamic characteristics of the surface are not altered.

In order to calculate the aerodynamic resistance  $r_a(x,t)$ , an approximate expression for the depth  $l$  (m) of the internal boundary layer in neutral flow conditions (Townsend, 1965; Blom & Wartena, 1969) is used:

$$l \{ \ln(l/z_0) - 1 \} = \kappa^2 x \tag{29}$$

where  $x$  (m) is the distance from the leading edge of the manured field measured

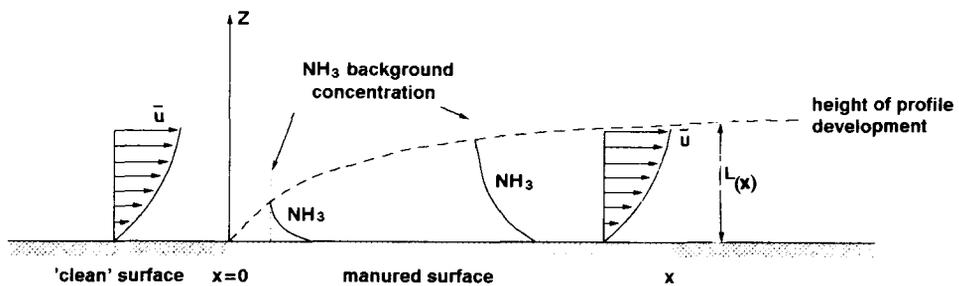


Fig. 2. Schematic representation of the development of the concentration profile of  $NH_{3(g)}$  over the manured field (adapted from Brutsaert, 1982).

in the direction of the mean wind and  $\kappa$  the von Karman constant ( $\kappa = 0.4$  (—)). It is known from internal boundary layer studies (e.g. Elliott, 1958; Jensen et al., 1984; Taylor & Lee, 1984; see Pasquill, 1972, for the analogy between diffusion of pollutants and internal boundary layer growth) that in neutral situations the wind profile inside the internal boundary layer is reasonably well approximated by the logarithmic form that satisfies the appropriate surface condition and the background concentration at  $z = l$ . For the aerodynamic resistance this implies:

$$r_a(x, t) = \ln(l/z_0) / \{\kappa \times u_*(t)\} \quad (30)$$

where  $u_*(t)$  is the friction velocity i.e. the scaling velocity of the logarithmic wind profile (see Appendix for the relation between  $u_*(t)$  and the wind profile). Since  $l$  increases with  $x$ ,  $r_a(x, t)$  increases also resulting in a decreasing volatilization rate  $R(t)$  as a function of  $x$ . The volatilization rate  $R(t)$  averaged over the field can be obtained by vertical integration of the net outflow ( $\int U (C - C_a) dz$  with  $U$  for wind speed) at the downstream edge of the field. Since  $R(t)$  decreases only slowly with  $x$ , a reasonable approximation is obtained by choosing  $r_a(x, t)$  and  $l$  at the downstream end of the field for the computation of the field averaged  $r_a(x, t)$  and  $R(t)$ . From  $x = 2.5$  m to  $x = 24$  m the resistance changes by no more than 25 %. Near the leading edge the errors are larger but in this area we cannot expect high accuracy because the assumption that  $l/x$  is small breaks down. In order to calculate  $r_a(L_x, t)$  with  $L_x$  as length of the field, from Equations 29 and 30,  $L_x$ ,  $z_0$  and  $u_*$  are required as input for the model.

It should be noted that the expressions above refer to neutral atmospheric flow in the surface layer. According to Monin-Obukhov similarity theory (e.g. Stull, 1988), this implies that  $l/|L|$  should be much smaller than 1, where  $L$  (m) stands for the Obukhov length. For an experimental field with a length  $L_x$  of 21.25 m (which was used to test the model), the internal boundary layer height  $l$  is 0.96 m at the downstream edge. This internal boundary layer is extremely shallow which justifies the neutral approximation because  $|L|$  is often larger than 5 m (except in cases with hardly any wind). However, to derive  $u_*(t)$  from wind observations at 10 m height it is often necessary to apply stability corrections to the logarithmic profile (see Appendix). For large fields and for very low wind speeds it might be necessary to apply stability corrections to the expressions for  $l$ ,  $r_a(x, t)$  and  $R(t)$  (see the Appendix for the appropriate expressions and for a more extensive discussion on stability effects).

Hardly any information exists on the value of the resistance  $r_b(t)$  of the quasi-laminar layer for  $\text{NH}_3(\text{g})$ . There is no reason to believe however that the behaviour of  $\text{NH}_3(\text{g})$  near the surface is different from other passive substances as water vapor and heat. The parameter  $r_b(t)$  is often specified by means of the integration constant  $z_{oc}$  (roughness length for concentration (m)) in the concentration profile. Brutsaert (1982) reviews data and theoretical values and concludes that  $z_0/z_{oc}$  is about 10, which means that:

$$r_b(t) = \ln(z_0/z_{oc}) / \{\kappa \times u_*(t)\} \sim 5.8/u_*(t) \quad (31)$$

The surface resistance  $r_s(t)$  represents the resistance of the surface itself and is the

result of the diffusion processes from inside the soil/slurry layer towards the air. The diffusion rate  $J_D(t)$  ( $\mu\text{g N m}^{-2} \text{s}^{-1}$ ) is defined by:

$$J_D(t) = D_{\text{aq}} \frac{(\bar{C}_{\text{aq}} - C_{\text{aq,s}})}{l_c} + D_g \frac{(\bar{C}_g - C_{\text{g,s}})}{l_c} \quad (32)$$

where  $\bar{C}_{\text{aq}}$  and  $\bar{C}_g$  are the average concentrations of ammoniacal N in the aqueous and the gaseous phase in the soil, respectively;  $C_{\text{aq,s}}$  and  $C_{\text{g,s}}$  are the ammoniacal-N concentrations in the same phases at the soil surface;  $l_c$  is the average distance (m) which the ammoniacal N has to bridge over to reach the surface ( $= 0.5 L_I$ ;  $D_{\text{aq}}$  and  $D_g$  are the soil-liquid and the soil-gas diffusion coefficients for ammoniacal N. Note that the soil-liquid diffusion coefficient is assumed to be the same for  $\text{NH}_3$  and  $\text{NH}_4^+$ . Substitution of Henry's law (Equation 26) in Equation 32 yields:

$$J_D(t) = D_{\text{aq}} K_h \frac{(\bar{C}_g - C_{\text{g,s}})}{l_c} + D_g \frac{(\bar{C}_g - C_{\text{g,s}})}{l_c} \quad (33)$$

or

$$J_D(t) = (D_{\text{aq}} K_h + D_g) \frac{(\bar{C}_g - C_{\text{g,s}})}{l_c} \quad (34)$$

where  $\bar{C}_g$  equals  $C_s(t)$  from Equation 2.

From the definition of  $r_s(t)$  it follows that the diffusion rate  $J_D(t)$  as expressed by Equation 34 can also be written as:

$$J_D(t) = \frac{1}{r_s(t)} (\bar{C}_g - C_{\text{g,s}}) \quad (35)$$

Combination of Equations 34 and 35 yields the following expression for  $r_s(t)$ :

$$r_s(t) = \frac{0.5L_I}{D_{\text{aq}} K_h + D_g} \quad (36)$$

where  $0.5L_I$  has been substituted for  $l_c$ , the average distance over which the ammoniacal N in the top compartment has to be transported to reach the soil surface. Henry's law constant  $K_h$  is calculated from Equation 27. The soil-liquid and the soil-gas diffusion coefficients are equalled to the water-liquid and the air-gas diffusion coefficient by multiplying by tortuosity factors to account for the reduced flow area and increased path length of diffusing ammoniacal N in soil. The tortuosity factors, which are functions of the volumetric moisture content, respectively the gas-filled pore volume, and the soil geometry, are described by the Millington-Quirk model (Jury et al., 1983). With this model we obtain the following expressions:

$$D_{\text{aq}} = (\theta_v^{10/3}/\phi^2) D_{\text{aq}}^{\text{water}} \quad (37)$$

$$D_g = (\theta_g^{10/3}/\phi^2) D_g^{\text{air}} \quad (38)$$

where  $D_{\text{aq}}^{\text{water}}$  and  $D_g^{\text{air}}$  are the water-liquid and the air-gas diffusion coefficients ( $\text{m}^2 \text{s}^{-1}$ ) and  $\theta_v$ ,  $\theta_g$  and  $\phi$  are the volumetric moisture content, the gas-filled pore volume and the porosity. Tabulated values of the water-liquid diffusion coefficient

as a function of temperature are given by Yuan-Hui & Gregory (1974); from these data the following expression was derived:

$$D_{\text{aq}}^{\text{water}} = 9.8 \times 10^{-10} \times 1.03^{(T-273)} \quad (39)$$

where  $T$  is the absolute temperature (K). A similar expression for the temperature-dependence of the air-gas diffusion coefficient was derived from the work of Bruckler et al. (1989):

$$D_{\text{g}}^{\text{air}} = 1.7 \times 10^{-5} \times 1.03^{(T-293)} \quad (40)$$

In order to calculate  $r_s(t)$  from Equations 36-40  $\theta_v$ ,  $\phi$  and  $T$  are required as input for the model.

With the above expressions for  $r_a(x,t)$ ,  $r_b(t)$  and  $r_s(t)$ , the description of the transfer function  $k(t)$  (Equation 28), in case of a field of limited size, is complete.

The computer program of the whole model was written in FORTRAN 77; it can be used on a VAX main frame and on a 640 K IBM-compatible PC. A listing of the program is available from the third author.

### Summary and conclusions

This paper presents a transfer model for  $\text{NH}_3$  volatilization from slurry. The model can be used to study the interaction of the chemical, physical and environmental factors influencing volatilization losses and their combined influence on  $\text{NH}_3$  volatilization under field conditions.

The model requires the following set of input data: the amount of ammoniacal N applied with the slurry and the initial depth of ammoniacal-N placement in the soil, the atmospheric  $\text{NH}_3$  background concentration, the type of adsorption isotherm to be used and the related constants, the aerodynamic roughness length of the surface, the distance from the leading edge of the manured field measured in the direction of the mean wind (the fetch), time-average values of bulk density and porosity of the top layer, time-dependent values of volumetric moisture content, friction velocity, soil temperature, pH, rainfall rate, evaporation rate and rate of net loss of ammoniacal N due to biological processes. The thickness of the top compartment has to be obtained from calibration of the model.

A third paper in this series about the experimental verification of the model is prepared by Chardon et al. As mentioned in the introduction, the model serves as the base for a predictive  $\text{NH}_3$  volatilization model. In order to proceed towards a predictive model the present model has to be extended to be able to predict the pH and the occurrence of biological processes (nitrification/denitrification, plant uptake) during a volatilization event.

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## Appendix

To solve the internal boundary layer problem for the emission of  $\text{NH}_3$  from a maturated field we have to solve the Equation that describes the balance between horizontal advection and vertical diffusion (this is an alternative to the more complicated trajectory-simulation model by Wilson et al., 1982):

$$U \frac{\partial C}{\partial x} = \frac{\partial}{\partial z} K \frac{\partial C}{\partial z} \quad (\text{A.1})$$

where  $C$  is the concentration,  $U$  the wind speed as a function of height  $z$ ,  $x$  the downstream distance from the leading edge of the field and  $K$  the diffusion coefficient as a function of  $z$ . The boundary conditions are:

$$\begin{aligned} C &= C_a & \text{for } x < 0 \text{ and } z \rightarrow \infty \\ C &= C_o & \text{for } x > 0 \text{ and } z = z_o \end{aligned} \quad (\text{A.2})$$

$$\text{with } C_o = C_s - R \times (r_b + r_s)$$

This problem can be solved to a reasonable degree of accuracy by assuming that a similarity solution exists. This means that the profile of  $C$  keeps the same form but that the scaling depends on  $x$ . The solution is assumed to be of the form:

$$\frac{C - C_a}{C_o - C_a} = f\left(\frac{z}{l}\right) \quad (\text{A.3})$$

where  $l$  is the internal boundary layer height. Scaling parameters  $C_o$  and  $l$  both vary with  $x$ , whereas  $f$  is a function of  $z/l$  only. This approach has been used by Townsend (1965) for the step in roughness and the step in surface temperature problems. A double step solution was computed by Blom & Wartena (1969). It has become recognized however, that the simple logarithmic interpolation between the new surface condition and the upstream value at  $z = l$  is almost as accurate as the similarity solution by Townsend (see Jensen et al., (1984) and Taylor & Lee (1984) for a discussion in the framework of wind energy applications). Since the simple empirical approach can easily be extended to non-neutral conditions we will employ it here instead of an explicit solution of Equation A.1.

The method, originally proposed by Elliott (1958) consists of the computation of an internal boundary layer height  $l$  as a function of  $x$  and the interpolation between the surface and the background concentration  $C_a$  at  $z = l$  with help of the profile functions that apply to homogeneous terrain (i.e. with stability correction functions added to the logarithmic form).

To compute the growth of the internal boundary layer we use the analogy as described by Pasquill (1972) between vertical diffusion of pollutants and internal boundary layer growth. The resulting expression reads (see van Ulden, 1978; van Wijk et al., 1989):

$$\frac{\partial l}{\partial x} = \frac{K(l)}{l \times U(l)} \quad (\text{A.4})$$

where  $K(l)$  and  $U(l)$  are the turbulent diffusion coefficient and the wind speed at height  $l$ . Expressions for  $K$  and  $U$  are:

$$K(l) = \frac{\kappa l u_*}{\phi_c(l/z)} \tag{A.5}$$

$$U(l) = \frac{u_*}{\kappa} \{ \ln(l/z_0) - \Psi_m(l/L) \} \tag{A.6}$$

The function  $\phi_c$  is the dimensionless concentration gradient in the surface layer (equal to the function for potential temperature and specific humidity) and  $\Psi_m$  is the stability correction function to the logarithmic wind profile. The Obukhov length  $L$  ( $= -u_*^3 T \rho_a C_p / \kappa g H_0$ ), with  $\rho_a$  for air density,  $T$  for absolute temperature,  $C_p$  for specific heat at constant pressure,  $g$  for the gravitational acceleration, and  $H_0$  for the surface heat flux) is the characteristic length scale that determines the stability of the atmospheric surface layer. The symbols  $u_*$  and  $\kappa$  represent the friction velocity and the von Karman constant ( $= 0.4$ ), respectively. We adopt the following expressions for  $\Psi_m$  and  $\phi_c$  and the stability correction function to the concentration profile,  $\Psi_c$ , as a function of  $z/L$  (see Dyer, 1974; van Ulden & Holtslag, 1985; Holtslag & de Bruin, 1988):

for  $L < 0$ :

$$\Psi_m = 2 \ln \left[ \frac{1+p}{2} \right] + \ln \left[ \frac{1+p^2}{2} \right] - \tan^{-1}(p) + \frac{\pi}{2} \tag{A.7}$$

$$\Psi_c = 2 \ln \left[ \frac{1+q}{2} \right] \tag{A.8}$$

with  $p = (1 - 16 z/L)^{1/4}$  and  $q = (1 - 16 z/L)^{1/2}$

$$\phi_c = (1 - 16 z/L)^{-1/2} \tag{A.9}$$

and for  $L > 0$ :

$$\Psi_m = \Psi_c = -0.7 \frac{z}{L} - (0.75 \frac{z}{L} - 10.72) \exp(-0.35 \frac{z}{L}) - 10.72 \tag{A.10}$$

$$\phi_c = 1 + 0.7 \frac{z}{L} + \frac{z}{L} (4.502 - 0.2625 \frac{z}{L}) \exp(-0.35 \frac{z}{L}) \tag{A.11}$$

The solution of A.4 in the surface layer can be approximated by (van Wijk et al., 1989):

$$l \left\{ \ln\left(\frac{l}{z_0}\right) - \Psi_m\left(\frac{l}{L}\right) - 1 \right\} \phi_c\left(\frac{l}{4L}\right) = \kappa^2 x \tag{A.12}$$

This implicit expression can be solved iteratively for specified values of  $z_0$ ,  $L$  and  $x$ . The functions  $\Psi_m$  and  $\phi_c$  are specified in Equations A.7, A.9, A.10 and A.11, where the functional dependence on  $z/L$  has to be replaced by  $l/L$  in  $\Psi_m$  and by  $l/(4L)$  in  $\phi_c$ . For  $l/L = 0$  this expression reduces to the neutral one used for small experimental fields with a very shallow internal boundary layer. The concentration profile in the internal boundary layer is assumed to be the equilibrium profile:

$$C - C_0 = \frac{-R}{\kappa u_*} \left\{ \ln\left(\frac{z}{z_0}\right) - \Psi_c\left(\frac{z}{L}\right) \right\} \quad (\text{A.13})$$

$$\text{with } C_0 = C_s - R(r_s + r_b)$$

Since the concentration at  $z = l$  has to match the background concentration  $C_a$ , we can solve for  $R$  and express the result in terms of an aerodynamic resistance:

$$r_a = \frac{1}{\kappa u_*} \left\{ \ln\left(\frac{l}{z_0}\right) - \Psi_c\left(\frac{l}{L}\right) \right\} \quad (\text{A.14})$$

For the averaged volatilization over the entire field, we again suggest applying the result for the downstream end of the field because the surface flux varies only slightly with  $x$ .

In summary, the following calculation procedure can be adopted, assuming that  $u_*$ ,  $z_0$ ,  $L$  and the length of the field  $L_x$  are known. First calculate the internal boundary layer height  $l$  from A.12 with  $x = L_x$  in an iterative way. The functions  $\Psi_m$  and  $\phi_c$  are specified in A.7 and A.9. When  $l$  is known,  $r_a$  follows directly from A.14 with  $\Psi_c$  as specified in A.8.

In practical situations the Obukhov length  $L$  and the friction velocity  $u_*$  are often not known. When these parameters are not available from direct measurements, we recommend using the methods developed by Holtslag & van Ulden (1983) and van Ulden & Holtslag (1985). They provide schemes that enable the estimation of  $u_*$  and  $L$  on the basis of routine observations of wind speed and cloud cover. A software implementation is described by Beljaars et al. (1989) and Beljaars & Holtslag (1989). The software package is freely available from the Royal Netherlands Meteorological Institute for research applications.

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# **Influence of different application rates of nitrogen to soil on rhizosphere bacteria**

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## **Abstract**

The bacterial populations in the rhizosphere of wheat were investigated with plants grown in soil at different nitrogen regimes. Nitrogen was applied to soil in different ways; two different levels of nitrogen (250 mg N per plant and 50 mg N per plant) were added as a single application or split in time during growth, and consequently smaller amounts were given each time. The different application methods made it possible to study the bacterial populations in relation to nitrogen concentrations in the roots and in the soil with comparable rates of plant biomass production.

When the nitrogen was applied as a single dose at the start of the experiment significantly larger total numbers of bacteria (colony forming units) were found in the rhizosphere of the plants than in the other treatments. This was correlated with higher nitrogen concentrations in the roots and with higher levels of extractable mineral nitrogen in the soil. In contrast, the numbers of fluorescent pseudomonads were smaller when a high nitrogen rate was applied once. Possible mechanisms for the observed changes in the microbial populations are discussed.

*Keywords:* wheat, rhizosphere bacteria, fluorescent pseudomonads, nitrogen fertilization

## **Introduction**

The larger numbers of microorganisms present in the rhizosphere compared to root-free soil is due mainly to the input of carbon substrates released from roots (Whipps & Lynch, 1986). In addition, several environmental factors influence both the release of materials from roots and the microbial utilization of these root-derived materials, and hence the abundance and composition of the microorganisms in the rhizosphere (Whipps & Lynch, 1986). Increased nitrogen fertilization has been reported to increase the numbers of bacteria in the rhizosphere (van Vuurde, 1978; Kolb & Martin, 1988; Liljeroth et al., 1990). Other authors have reported no effect of nitrogen on bacterial populations in the rhizosphere (van Vuurde & de Lange, 1978; Turner et al., 1985).

Increased nitrogen availability in soil could improve utilization efficiency of the

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exudates by microorganisms (Merckx et al., 1987; van Veen et al., 1989; Liljeroth et al., 1990) since, in the rhizosphere, new carbon is continuously added by the roots in an environment where the plant and the microorganisms are continuously competing for nutrients. In these studies, plants appeared to be strong competitors for nutrients compared to the microorganisms. Since nutrients, such as nitrogen, are essential in both plant and microbial metabolism, competition for nitrogen could affect microbial carbon transformation and thus the processes ultimately linked to microbial biosynthesis and energy production.

Another reason for changes in microbial populations in the rhizosphere in response to nitrogen additions could be altered root exudation, but few studies on the effect of nitrogen on root exudation have been published. Bowen (1969) reported that loss of amino acids from the root of *Pinus radiata* seedlings was reduced by nitrogen deficiency but increased by phosphorus deficiency. Using  $^{14}\text{C}$ -labelling of atmospheric  $\text{CO}_2$ , Liljeroth et al. (1990) found that more of the root-translocated carbon was released from wheat roots of plants grown at high soil nitrogen levels than at low soil nitrogen levels.

In this study the effects of two different levels of nitrogen fertilization on the dynamics of the bacterial populations in the rhizosphere were investigated. The nitrogen was applied in two different ways, i.e. a single application or split application. The different application methods made it possible to study the bacterial populations in relation to nitrogen concentrations in the roots and in the soil with comparable rates of plant biomass production.

## Materials and methods

### *Soil*

A loamy sand (Ede) was air-dried to 10 % water content and passed through a 5-mm sieve. Mineral nutrients and water were added; the final water content was 14 % ( $-25.1$  kPa). Plastic pots were filled with 1.5 kg soil. Mineral nutrients, except nitrogen, were applied in the following amounts (mg per pot): P and K, 191 and 407, as  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{KH}_2\text{PO}_4$ , respectively; Cu 3.4 as  $\text{CuSO}_4$ ; B 0.8 as  $\text{H}_3\text{BO}_3$ ; Mo 5.5 as  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ; Mn 1.4 as  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ; Zn 1.1 as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ; Fe 2.5 as Fe-EDTA. Half of this nutrient mixture was thoroughly mixed with the soil before filling the pots and the remaining part was added with the irrigation water after 5 weeks of plant growth. Four nitrogen fertilization treatments were used:

- (I) 250 mg N per plant applied once,
- (II) 50 mg N per plant applied once,
- (III) 250 mg N per plant, multiple applications (split treatment),
- (IV) 50 mg N per plant, multiple application.

The split treatments followed an exponentially increasing addition rate up to 48 days of plant growth as described in Table 1. The nitrogen given at the start of the experiment was thoroughly mixed with the soil together with the other nutrients; nitrogen added later was given with the irrigation water.

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Table 1. Nitrogen additions to the soil in four different treatments: high/low N and single/split application (mg N per pot as  $\text{NH}_4\text{NO}_3$ ).

Day	Treatment			
	I high N single appl.	II low N single appl.	III high N split appl.	IV low N split appl.
0	250	50	0	0
7	0	0	4	0.8
14	0	0	5	1.0
21	0	0	7	1.4
24	0	0	4	0.8
28	0	0	6	1.2
31	0	0	9	1.8
35	0	0	17	3.4
38	0	0	18	3.6
42	0	0	35	7.0
45	0	0	37	7.4
48	0	0	71	14.2
55	0	0	37	7.4
Sum	250	50	250	50

*Plants and growing conditions*

Seeds of spring wheat (*Triticum aestivum* L. emend Thell., line C-R5B) were germinated on moist filter paper and then planted in pots (one plant per pot). The surface of the soil was covered with a layer of washed aquarium grit. Unplanted pots of all nitrogen addition treatments were prepared as controls. The moisture content of the soil was adjusted daily to 14 % by weighing the pots and adding sterilized demineralized water. All pots were incubated in a growth chamber at 20 °C and a relative humidity of 70 % during the day (16 h). During the night (8 h), the temperature and relative humidity were 15 °C and 85 %, respectively. The light intensity was approximately  $650 \mu\text{E m}^{-2} \text{s}^{-1}$ . After 20, 27, 34, 47 and 67 days of incubation, three plants of each treatment were harvested and soil samples were taken for bacterial and nitrogen analysis. Two samples per treatment were taken from the soils of the unplanted controls.

*Analyses*

Bacterial numbers in the rhizosphere and unplanted soil were determined with plate count methods. After separating the root system from the soil the roots were shaken free of loosely adhering soil and root samples (10 g) with soil still adhering, representing the whole root system, were placed in Erlenmeyer flasks containing 95 ml 0.1 % sterile sodium pyrophosphate solution and 10 g grit and shaken on a rotary shaker for 10 minutes at 200 rpm. Tenfold serial dilutions of the suspensions

were made with 0.1 % sodium pyrophosphate and plated out on culture media. Root-free soil samples of 10 g were also taken and treated in the same way. When the dilutions were made the roots were removed from the Erlenmeyer flasks and washed in running tap water; root weight was determined and the actual weight of the soil used for the suspension was then calculated. Total plate counts were made on 1/10-strength Tryptic Soya Agar (TSA) (Martin, 1975) and the numbers of fluorescent pseudomonads were counted on medium S1 (Gould et al., 1985). The TSA plates were incubated for 10 days at 20 °C while the S1 plates were counted after an incubation of four days at 24 °C.

Dry weights of shoots, roots and soil were determined after drying at 80 °C to constant weight. Nitrogen contents of homogenized plant material were determined after digestion of plant material in sulphuric acid and salicylic acid. The amount of nitrogen was determined as  $\text{NH}_4^+$  with Nessler's reagent (van Ginkel & Sinnaeve, 1980). The presence of mineral nitrogen in soil was determined by extraction of 25 g soil (two replicates per pot) with 50 ml 0.5 M  $\text{K}_2\text{SO}_4$  on a rotary shaker for one hour. After centrifugation at 18 000 rpm for 10 minutes, samples were taken for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  analysis. Nitrogen analyses were carried out with an autoanalyzer according to van Ginkel & Sinnaeve (1980).

#### *Statistical analyses*

A two-factor analysis of variance over the entire time of the experiment was performed with time and nitrogen treatments as the factors. Bacterial numbers were log-transformed.

### **Results**

#### *Plant growth*

Growth of shoots and roots was similar for treatments I (high N, single application) and II (low N, single application) up to 34 days. Thereafter, the plants in treatment I grew faster. The plants given nitrogen as split applications (III, IV) grew slower up to 34 days. However, in the later stages of the experiment, the growth rates of the plants in treatment III (high N, split application) were slightly higher than those of plants in treatment I (Table 2). Thus, growth appeared to have been limited by nitrogen supply in the early stage for the split application treatments. Plants with the high nitrogen treatment (I en II) generally had higher shoot-root ratios than plants with the low nitrogen treatments (II en IV).

#### *Plant nitrogen content*

The nitrogen concentrations in shoots and roots decreased with time ( $P < 0.001$ , Table 3). The decrease was smaller in the two treatments with split application, i.e. III and IV, than in single application treatments, as indicated by a significant interaction between time and nitrogen treatment ( $P < 0.001$ ). The plants in treatment

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Table 2. Dry weight of shoots and roots of spring wheat at five harvest times. Means  $\pm$  SD (g per plant) are given.

Day		Treatment <sup>1</sup>				LSD ( $P < 0.05$ )
		I	II	III	IV	
20	shoot	0.56	0.58	0.47	0.39	0.11
	root	0.16	0.17	0.17	0.17	0.06
27	shoot	1.68	1.54	1.15	0.71	0.41
	root	0.55	0.62	0.56	0.36	0.24
34	shoot	3.66	3.60	2.28	1.56	0.77
	root	1.27	1.26	0.96	0.70	0.23
47	shoot	8.85	6.46	6.18	3.04	0.61
	root	1.92	1.61	1.22	0.72	0.31
67	shoot	15.18	7.73	12.39	5.79	0.76
	root	2.38	1.50	2.03	0.92	0.16

<sup>1</sup> See table 1.

I usually had higher nitrogen concentrations both in the shoots and the roots than the plants in all the other treatments. The concentrations of plant nitrogen were generally higher in treatment III than in treatment IV. In treatment II, the concentrations were initially comparable to I but decreased quickly and by the end of the experiment, the plant nitrogen concentrations were the lowest of all treatments. pH of the soils (bulk soil of planted pots) was measured on day 67 and only minor differences could be detected among treatments: 6.1 and 6.4 for high N and low N, respectively.

Table 3. Nitrogen concentrations in shoots and roots of spring wheat (percent of plant dry weight).

Day		Treatment <sup>1</sup>				LSD ( $P < 0.05$ )
		I	II	III	IV	
20	shoot	4.0	4.8	4.0	3.3	1.2
	root	3.9	3.3	2.5	2.0	0.4
27	shoot	4.4	2.5	2.3	2.2	0.9
	root	3.4	1.7	1.5	1.7	0.7
34	shoot	2.7	1.3	1.8	1.2	0.2
	root	2.8	1.0	1.3	1.0	0.3
47	shoot	1.6	0.7	2.2	1.2	0.2
	root	1.8	0.8	1.5	1.0	0.3
67	shoot	1.0	0.9	1.3	0.8	0.6
	root	1.5	0.7	1.7	1.0	0.3

<sup>1</sup> See Table 1.

Table 4. Extractable nitrogen in soil at five harvest times (mg N per kg soil).

Day		Treatment <sup>1</sup>			
		I	II	III	IV
20	NH <sub>4</sub> -N	47 ± 12	<2	<2	<2
	NO <sub>3</sub> -N	33 ± 6	9 ± 9	<2	<2
27	NH <sub>4</sub> -N	7 ± 11	<2	<2	<2
	NO <sub>3</sub> -N	84 ± 3	<2	<2	<2
34	NH <sub>4</sub> -N	<2	<2	<2	<2
	NO <sub>3</sub> -N	32 ± 3	<2	<2	<2
47	NH <sub>4</sub> -N	30 ± 3	<2	7 ± 1	<2
	NO <sub>3</sub> -N	5 ± 1	<2	7 ± 1	<2
67	NH <sub>4</sub> -N	29 ± 2	2 ± 3	25 ± 2	<2
	NO <sub>3</sub> -N	<2	<2	<2	<2

<sup>1</sup> See Table 1.

### *Extractable nitrogen in soil*

The amount of extractable nitrogen in soil (NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) was generally much larger in treatment I than in all the other treatments ( $P < 0.001$ , Table 4). In treatments II and IV, extractable nitrogen was not usually detectable while in treatment III the levels increased towards the end of the experiment. At the second and third harvest, i.e. day 27 and day 34, nitrogen was mainly found in the form of NO<sub>3</sub><sup>-</sup>, while on days 47 and 67 NH<sub>4</sub><sup>+</sup> was also found. At the first harvest, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were found in comparable amounts.

### *Bacteria*

In the unplanted control soil no significant differences in total colony-forming units (CFU) were found among the treatments (Fig. 1b) although the numbers of fluorescent pseudomonads found in the unplanted controls were smaller in treatment I than in the other treatments (Fig. 2b,  $P < 0.001$ ). In the rhizosphere, however, significantly larger total numbers of bacteria were found in treatment I ( $P < 0.001$ ), while the other treatments did not differ significantly (Fig. 1a). The differences became evident after 34 days of plant growth. The numbers of fluorescent pseudomonads in the rhizosphere were, in contrast to the total CFU, lower in treatment I than in the other treatments (Fig. 2a,  $P < 0.01$ ). The percentage fluorescent pseudomonads of the total CFU was always lower than 0.2% and decreased with time both in the unplanted soil and in the rhizosphere ( $P < 0.05$ ) and the percentages fluorescent pseudomonads of the total CFU were significantly lower in treatment I ( $P < 0.05$ ) than in other treatments.

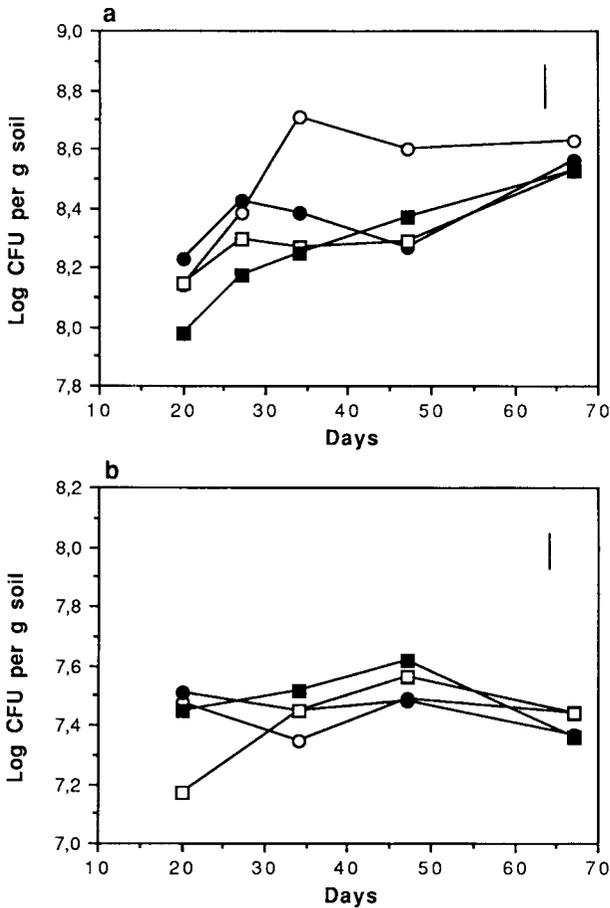


Fig. 1. Bacterial numbers (total CFU) in the rhizosphere of wheat (a) and in root-free control soil (b) at different nitrogen regimes. Symbols —○— high N single application; —●— low N, single application; —□— high N, split application; —■— low N, split application. Bars indicate standard deviation from ANOVA.

## Discussion

The plants grew faster in treatment I, although this became only evident after 27 days. In treatment III (high nitrogen, split application), growth was slower in the beginning of the experiment, indicating nitrogen limitation. The aim of the exponentially increased addition rate of nitrogen with time in treatment III was to give the plant the nitrogen needed for growth while avoiding high soil nitrogen concentrations. It can be concluded that a higher addition rate would have been necessary for optimum growth. Nevertheless, by adding nitrogen in different ways it was possible, at least during part of the growing period, to create plants with comparable

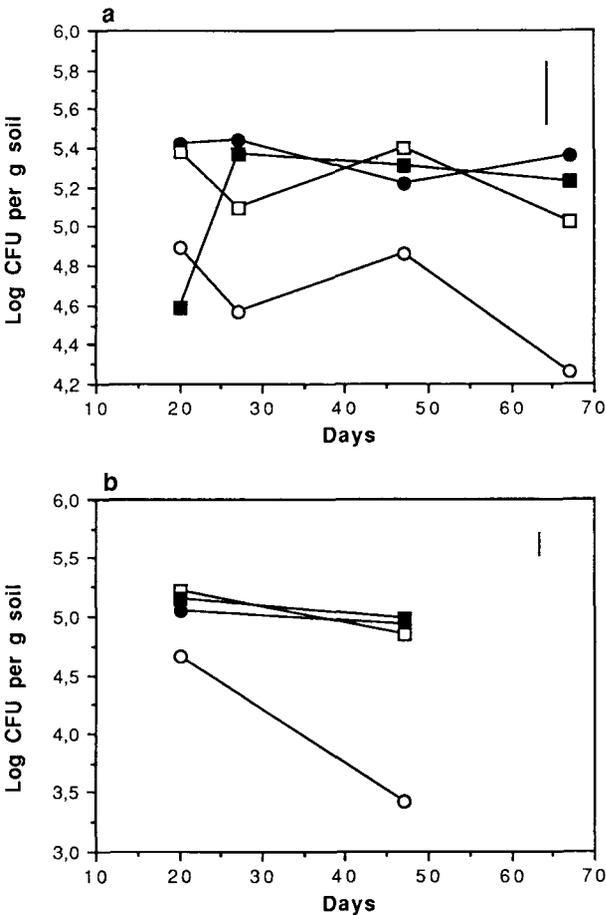


Fig. 2. Numbers of fluorescent pseudomonads in the rhizosphere of wheat (a) and in root-free control soil (b) at different nitrogen regimes. Symbols: —○— high N, single application; —●— low N, single application; —□— high N, split application; —■— low N, split application. Bars indicate standard deviation from ANOVA.

dry weight production but with different concentrations of nitrogen both in the plants and in soil.

The total numbers of bacteria were significantly higher in the treatment in which nitrogen was applied at the higher rate in a single dose (I) than in any other treatment. In this treatment the concentrations of nitrogen were considerably higher both in the roots and in the soil during the main part of the experimental period. It is difficult to conclude from the results which mechanisms led to the higher 'total' bacterial numbers, a higher exudation rate or improved microbial utilization of the exudates, since more mineral nutrients were available (extractable) in the soil. Qualitative changes in root exudation may also have occurred.

Recently, indications of mineral nutrient limitations of microbial metabolism in the rhizosphere have been reported (Merckx et al., 1987; van Veen et al., 1989; Liljeroth et al., 1990). In experiments where plants were grown in  $^{14}\text{C}$ -labelled  $\text{CO}_2$  atmosphere, Merckx et al. (1987) found that in a nutrient-poor treatment, a greater proportion of  $^{14}\text{C}$  accumulated in soil after 6 weeks, and a higher percentage of the soil  $^{14}\text{C}$  residue remained in an easily extractable (or available) form, suggesting mineral nutrient limitation for microbial growth. The decomposition of glucose, added to soil, was found to be stimulated by higher mineral nutrient levels (van Veen et al., 1989), while the decomposition rate of added straw, as measured by  $\text{CO}_2$  production, appeared to be negatively influenced by high nutrient levels. Thus, their data agree with the present results that larger amounts of available mineral nitrogen in soil stimulate microbial metabolism in planted soil.

While the total number of bacteria, counted on a relatively poor medium, were larger at higher nitrogen concentrations, the numbers of fluorescent pseudomonads were significantly smaller. This effect was evident both in the rhizosphere soil and in the unplanted control soil, indicating a direct effect of nitrogen on these bacteria. Perhaps some groups of bacteria are sensitive to high ionic concentrations. This result is contradictory to the increased numbers of fluorescent pseudomonads found by Merckx et al. (1987) in the rhizosphere of maize at a higher level of additions of mixed mineral nutrients as compared to soils to which a smaller amount of mineral nutrients was applied. However, in the latter study the actual concentrations of mineral nutrients in the soil were not measured. It is possible that the maize plants quickly took up the nutrients and that high soil concentrations occurred only during a short initial period. Besides, root-derived materials may be qualitatively different for maize and wheat. Materials released from maize contain greater proportions of simple sugars, which are readily available substrates for the metabolism of quickly growing bacteria such as fluorescent pseudomonads. Merckx et al. (1986, 1987) showed that root-derived products from maize were more efficiently utilized than products from wheat roots.

In a paper by Miller et al. (1990) the general behaviour of fluorescent pseudomonads was studied in the rhizosphere of two wheat cultivars. The percentages of fluorescent pseudomonads of the total numbers were always  $< 1\%$  and decreased significantly with time. Further, the percentages were lower in the rhizoplane than in the rhizosphere soil. A similar decrease with time was observed here and generally the percentages were even lower in the rhizosphere soil than in the root-free soil. These results indicate that fluorescent pseudomonads are not the most rhizosphere-competent group of bacteria since other groups of bacteria apparently increase in numbers and as a percentage of the total populations proposed by Miller et al. (1990).

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# Nitrogen cycling in high-input versus reduced-input arable farming

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## Abstract

A comparison is made of a high-input and two reduced-input farming systems with a rotation of winter wheat — sugar beet — spring barley — potatoes on a calcareous silt loam soil. Nitrogen balance sheets for the growing seasons of 1986-1988 showed N deficits of 0-170 kg ha<sup>-1</sup>, suggesting substantial N losses to the environment.

The uncertainty about actual N losses mainly depended on the uncertainty of estimated net N mineralization. Periods with much rainfall in 1987 and 1988, inappropriate use of animal manure and soil compaction may partly account for the heavy N losses in all three farming systems. Potential rates of N-cycle processes were studied over the years to observe effects of changes in management. To increase the efficiency of mineral and organic N inputs, and to decrease N losses, soil inorganic-N concentrations should be kept low, especially in periods when losses are likely to occur.

*Keywords:* N balance, N cycling, N mineralization, N immobilization, denitrification, microbial biomass

## Introduction

The following problems with high-input arable farming in the Netherlands led to the establishment of the Dutch Programme on Soil Ecology of Arable Farming Systems (Brussaard et al., 1988):

- contamination of groundwater by nitrate and of the atmosphere by NH<sub>3</sub> and possibly N<sub>2</sub>O due to high inputs of fertilizers and manures,
- high costs and unwanted environmental effects due to abundant use of chemicals for crop protection, weed control and soil fumigation,
- deterioration of soil structure due to the use of heavy machinery, which necessitated intensive soil tillage.

The Programme's hypothesis is that a change from 'conventional' (high input) to 'integrated' (reduced input) farm management can improve:

- nutrient use efficiencies,

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Communication No 30 of the Dutch Programme on Soil Ecology of Arable Farming Systems.

- control of pests, diseases and weeds,
- soil structure, with fewer negative effects on the environment.

Integrated management might give lower crop yields than conventional management, but because of lower costs the profitability to the farmer could be similar.

Agroecosystems are inherently more 'leaky' than undisturbed natural ecosystems, where vegetation is continuously present. Increased inputs of nitrogen into agriculture have greatly increased crop (N) outputs, but they have also increased N losses to the environment (Kolenbrander, 1982). N losses to the environment may increase strongly when N fertilization becomes higher than a certain threshold value, often near the optimum for crop production (Prins et al., 1988). The risk of N losses to the environment can be reduced by avoiding peak concentrations of inorganic N ( $N_i$ ) in soil, e.g. by split application of fertilizer. When  $N_i$  fertilization of crops is decreased and partially replaced by organic manures, N mineralization by soil organisms becomes more important for the N supply of the crops (Lopez-Real, 1986). Use of organic manure will increase the pool of labile soil organic N; losses of N mineralized from this pool should be avoided by using green manures and by stimulating N immobilization during periods with little or no N uptake by a crop.

In this paper,  $N_i$ -balance calculations covering the growing season will be discussed as well as changes in soil N mineralization rate, in N uptake by the crop, and in N losses due to changes in management. A conventional farming system was compared with two integrated systems, each system with the same rotation of winter wheat, sugar beet, spring barley and potatoes on a silt loam soil. The main differences in management are given in Table 1 (Brussaard et al., 1988; Kooistra et al., 1989). Soil physical conditions and meteorological data necessary to account for some of the differences in overall N budget will be discussed.

Table 1. Main differences between 'conventional', 'integrated' and 'integrated with minimum tillage' management systems.

	Conventional	Integrated	Integrated with minimum tillage
Inorganic N fertilization	As $Ca(NO_3)_2$	Less than conventional	As integrated
Organic N fertilization	Crop residues only	Crop residues, manure/compost	As integrated
Crop protection	Conventional use of pesticides including soil fumigation	Less than conventional; no soil fumigation	As integrated, but more use of herbicides
Tillage	20 or 25 cm ploughing	12 to 15 cm ploughing plus subsoiling to 20 or 25 cm	5 cm ploughing or 10 cm cultivator

**Materials and methods**

*Field data*

Field work was carried out at the experimental farm Dr H. J. Lovinkhoeve on a calcareous silt loam soil. Soil characteristics of the 0-25 cm layer were: pH-KCl 7.5; organic matter 2.2-2.8 %; total N 0.10-0.14 %; CaCO<sub>3</sub> 9 %, sand 12 %, silt 68 %, clay 20 %. Average annual rainfall during 1943-1987 was 730 mm. A previous experiment at the experimental site, in which three different input regimes of organic matter (A, B and C) were compared, was taken as a starting point. During the period 1966-1984, average annual inputs of organic matter were 5650 kg ha<sup>-1</sup> for variant A (crop residues, including ploughing down of a grass ley, and applications of farmyard manure), 3200 kg ha<sup>-1</sup> for variant B (crop residues only) and 5280 kg ha<sup>-1</sup> for variant C (crop residues and green manures). As a result, during 1981-1984 the A, B and C blocks had average organic matter contents of 2,8 %, 2,2 % and 2,3 %, respectively. Four new variants were started in autumn 1985: conventional management on 50 % of block A (CONVA) and on 50 % of block B (CONVB), and integrated management on 50 % of block A (INTA) and on 50 % of block B (INTB). In autumn 1986, integrated management with minimum tillage was started on block C (MTC) as a fifth variant (Fig. 1). All variants had the same crop rotation of winter wheat — sugar beet — spring barley — potatoes. Each variant or treatment consisted of four fields of 12 × 85 m<sup>2</sup>, with each crop of the rotation being present each year in every variant. The MTC variant was started in duplicate, i.e. on eight fields, but because of nematode problems four fields (Nos 10-13) had to be disinfested and were returned to conventional practice in 1989. Every year

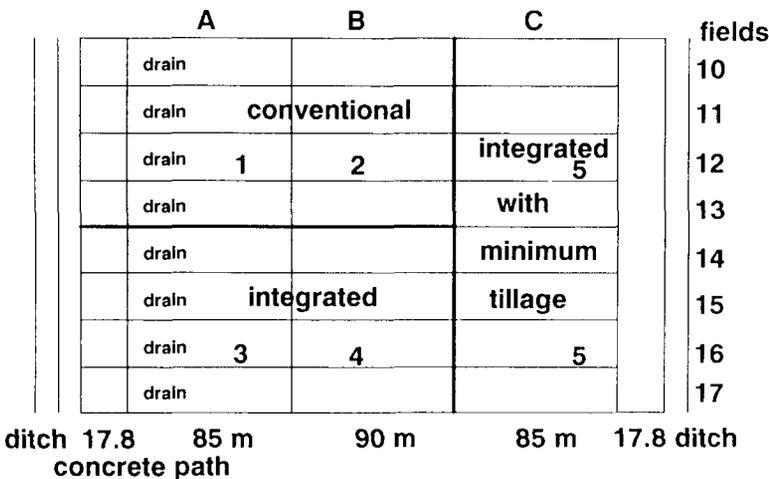


Fig. 1. The position of the new variants laid on the A, B, and C blocks of a previous long-term experiment, which had resulted in organic matter contents of about 2.8 %, 2.2 % and 2.3 % for block A, B and C, respectively.

for each field, crop yields and total-N contents of consumable and other plant parts were determined at harvest.

Detailed research work was done mainly on the variants CONVB and INTA (fields 12B and 16A). We expected only small changes in soil organic matter (SOM) and labile N pools of these variants, since the organic matter input would be changed little under the new management. The other variants, CONVA and INTB, were expected to show larger changes in their SOM and labile N pools and to reach new equilibrium levels after several years. Table 2 shows the recent cropping history of six fields studied, as well as their organic matter and total-N contents.

The following parameters were determined:

- dry matter and total-N content of the crop by harvesting two or three subplots (3-16 m<sup>2</sup>, 4 or 5 times during the growing season);
- mineral N extractable with 1 M KCL, in six layers of the soil profile down to 1 m, at the experimental harvesting dates; extracts were analysed using a Technicon autoanalyzer (Traacs 800); dichromate-oxidizable organic matter according to Kurmies, and total-N contents according to Deijs, annually in the layers 0-10, 10-25 and 25-40 cm;
- meteorological parameters and soil physical conditions;
- root development (van Noordwijk, 1987).

N fertilization of conventional fields served to increase the amount of mineral N present in spring in the upper 60 cm (for winter wheat 100 cm) of the soil to the level needed by the crop (Neeteson, 1989); it was often split over two or even three dressings.

Integrated fields received less N and part of it as organic manure (Fig. 4); the solid fraction of pig slurry (20 t ha<sup>-1</sup>, containing 24 % dry matter and 0.85 % total N) was applied in the spring of 1987 to potato and sugar beet fields, and spent

Table 2. Recent cropping history, soil organic matter and total-N contents of six fields used in detailed studies. See Fig. 1 for the layout of the experiment.

Field	Variant <sup>1</sup>	Year						Organic matter content <sup>2,3</sup> (%)	Total N <sup>2</sup> (%)
		84	85	86	87	88	89		
12A	CONVA	l <sup>4</sup>	p	ww	sb	b	p	2.75	0.14
12B	CONVB	p	sb	ww	sb	b	p	2.20	0.10
16A	INTA	p	sb	ww	sb	b	p	2.75	0.14
16B	INTB	ww	f	ww	sb	b	p	2.30	0.11
12C	MTC	p	sb	b	sb	b	p	2.35	0.11
16C	MTC	ww	f	p	sb	b	p	2.35	0.11

<sup>1</sup> Variants: CONVA = conventional management on block A, CONVB = conventional management on block B, INTA = integrated management on block A, INTB = integrated management on block B, MTC = integrated management with minimum tillage on block C.

<sup>2</sup> Average 1981-1984, 0-25 cm layer.

<sup>3</sup> Organic matter = 1.724 × oxidizable organic 'C'.

<sup>4</sup> p = potatoes, sb = sugar beet, ww = winter wheat, b = spring barley, l = grass ley, f = flax.

mushroom compost (30 t ha<sup>-1</sup>, containing 35 % dry matter and 0.7 % total N) was applied in the autumn of 1987 and 1988 on fields where sugar beet were grown in 1988 and in 1989, respectively; in spring 1989, a granular organic fertilizer (3 t ha<sup>-1</sup>, containing 78 % dry matter and 2.1 % total N) was applied to potato fields. The applied pig slurry solids, compost and granular organic fertilizer contributed per ha 3700, 5300, and 1800 kg organic matter, and 170, 210 and 60 kg N (mainly organic N), respectively.

#### *Inorganic-N (N<sub>i</sub>) balance calculations*

In the soil system the following balance applies:

$$\text{Sum of } N_i \text{ inputs} = \text{sum of } N_i \text{ outputs} + \Delta N_i - \text{soil} \quad (1)$$

where  $\Delta N_i$  is the change in inorganic-N content of the soil.

Inputs can be fertilizer N<sub>i</sub>, N<sub>i</sub> in precipitation, N<sub>i</sub> in manure, or N<sub>i</sub> from N mineralization. Outputs can be the N<sub>i</sub> taken up by the crop, by green manures or by weeds, N<sub>i</sub> losses to the environment (volatilization of NH<sub>3</sub>, denitrification and leaching) and immobilization of N<sub>i</sub> in soil organic matter.

Inputs to compensate (estimated) outputs should take into account N<sub>i</sub> supplied to the crop by net mineralization of soil organic N or, in certain cases, the net immobilization of N<sub>i</sub>.

All calculations are based on field and laboratory measurements described in this paper, except for N<sub>i</sub> in precipitation, for which data from a nearby weather station have been used.

#### *Laboratory studies*

In laboratory experiments, the mechanisms of some of the processes involved were investigated in more detail:

— Potential N-mineralization rates were measured by incubating moist homogenized soil samples for 1, 6 or 12 weeks (duplicates per soil layer), taken 4 or 5 times a year, including the experimental harvesting dates. Before and after incubation, samples were extracted with 1 M KCl and analysed for mineral N (ammonium and nitrate) using standard autoanalyzer methods. The increase in mineral N from 1 to 6 or 12 weeks incubation was used to calculate N-mineralization rates. Mineral N after 1 week incubation is taken as the reference to compensate for a possible effect of homogenizing the samples. The soil samples were also used to determine N flushes by chloroform fumigation followed by 10 days incubation at 25 °C (Jenkinson & Powlson, 1976). The N flush, the difference in mineral N after incubation between fumigated and unfumigated control samples, was used as an estimate of N in microbial biomass.

— Separately, the effect of temperature on N mineralization was established by incubation of samples at 5, 10 and 20 °C.

— Potential N-mineralization rates of organic manures were also measured by incubating them with homogenized moist soil at 5, 10 and 20 °C.

— Structurally intact soil cores of 100 cm<sup>3</sup>, taken from the 0-5 cm layer in the field, were incubated at 20 °C in closed 370-cm<sup>3</sup> jars to measure potential O<sub>2</sub> consumption rates. Sugar beet fields 12B, 12C, 16A and 16B were sampled four times from May to October 1987; eight samples were taken per field each time. Structurally intact soil cores of 0.75-1.0 dm<sup>3</sup>, taken from the 0-13 cm layer of fields 12C and 16A with steel cylinders with a cutting edge, were incubated in closed pots of about 1.5 dm<sup>3</sup> to measure potential O<sub>2</sub> consumption and denitrification rates; 4 or 6 replicates were used at 3 sampling dates in 1987. Samples (5 cm<sup>3</sup> of the headspace gases) were taken with a syringe through a septum and analysed by gas chromatography (for O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub>). The production of N<sub>2</sub>O, in the presence of added C<sub>2</sub>H<sub>2</sub> (to a partial pressure of about 1 kPa) as an inhibitor of N<sub>2</sub>O-reductase, was used as a measure of denitrification (Kroeze et al., 1989).

## Results and discussion

### *Inorganic-N balance calculations*

The N<sub>i</sub> balance for winter wheat in 1986 showed a deficit of about 50 kg ha<sup>-1</sup> for field 16A (INTA), presumably lost by denitrification, and none for field 12B (CONVB). This loss of N occurred probably in June, when crop demand for N was highest, and may account for the lower N output for field 16A. A very dry period in August 1986 caused early senescence of the crop and limited its further N uptake, whereas N mineralization continued which accounted for the amount of soil nitrate present at harvest, N<sub>c</sub> (Fig. 2a). N<sub>i</sub> balances for sugar beet in 1987 and for spring barley in 1988 showed large deficits (Fig. 2b, c), presumably losses due to nitrate leaching as well as denitrification and perhaps NH<sub>3</sub> volatilization. Both 1987 and 1988 were very wet years (Fig. 3), which may largely account for the heavy N losses. In June 1987 and in July 1988, groundwater levels rose to 20-40 cm below the soil surface. Soil bulk densities of the 0-40 cm layers were relatively high in 1987 as well as in 1988, which may have furthered denitrification.

N losses early in the growing season make the crop more dependent on N supply from mineralization than in other years. Crops under integrated management may in such cases profit more from N supply by mineralization than crops under conventional management. When net N mineralization was overestimated, the N deficit overestimated the N losses.

### *N uptake, N removal and N recycling*

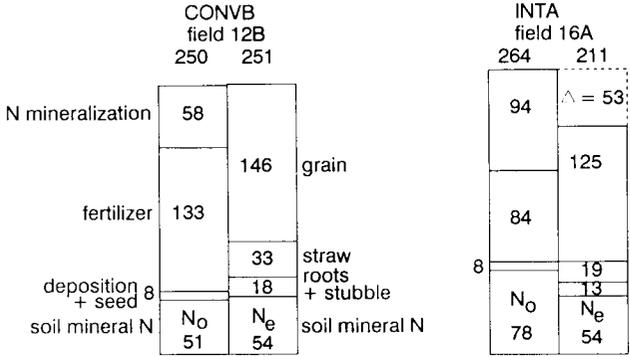
The amounts of nitrogen removed from the fields in the harvested products (grain and straw, beets and tubers) are shown in Figure 4, which also gives the amounts of inorganic and organic N applied. Although the amounts of N removed by specific crops in 1987 were quite different from those in 1988, the total amounts of N removed with the four crops were similar in these years for each of the five variants. Substantial amounts of N taken up by the crops and by green manures were returned to the soil as crop residues (roots, stubble, foliage, beet tops). N removal at harvest

NITROGEN CYCLING IN ARABLE FARMING SYSTEMS

N balance (kg/ha)

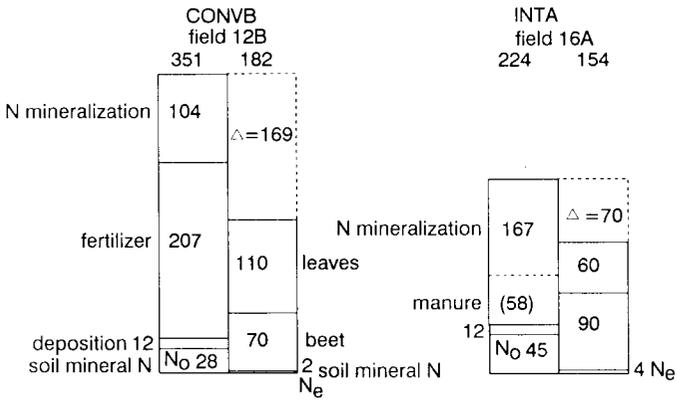
winter wheat 20/4-19/8/1986

a



sugar beet 18/2-27/10/1987

b



spring barley 18/2-9/8/1988

c

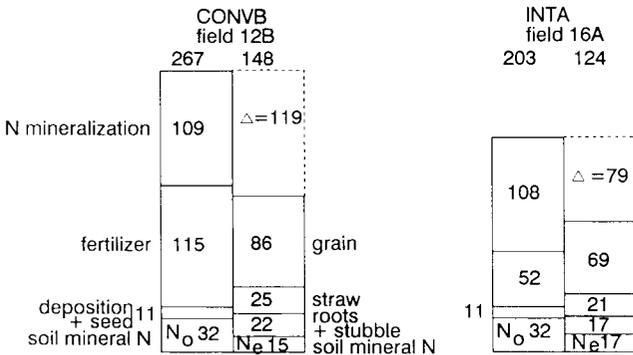


Fig. 2. Nitrogen balance sheets for field 12B under conventional management (CONVB) and for field 16A under integrated management (INTA). (a) Winter wheat (1986). (b) Sugar beet (1987). (c) Spring barley (1988).  $N_o$  = soil mineral N at the start,  $N_e$  = soil mineral N at the end of the balance period, in the 0-100 cm layer.

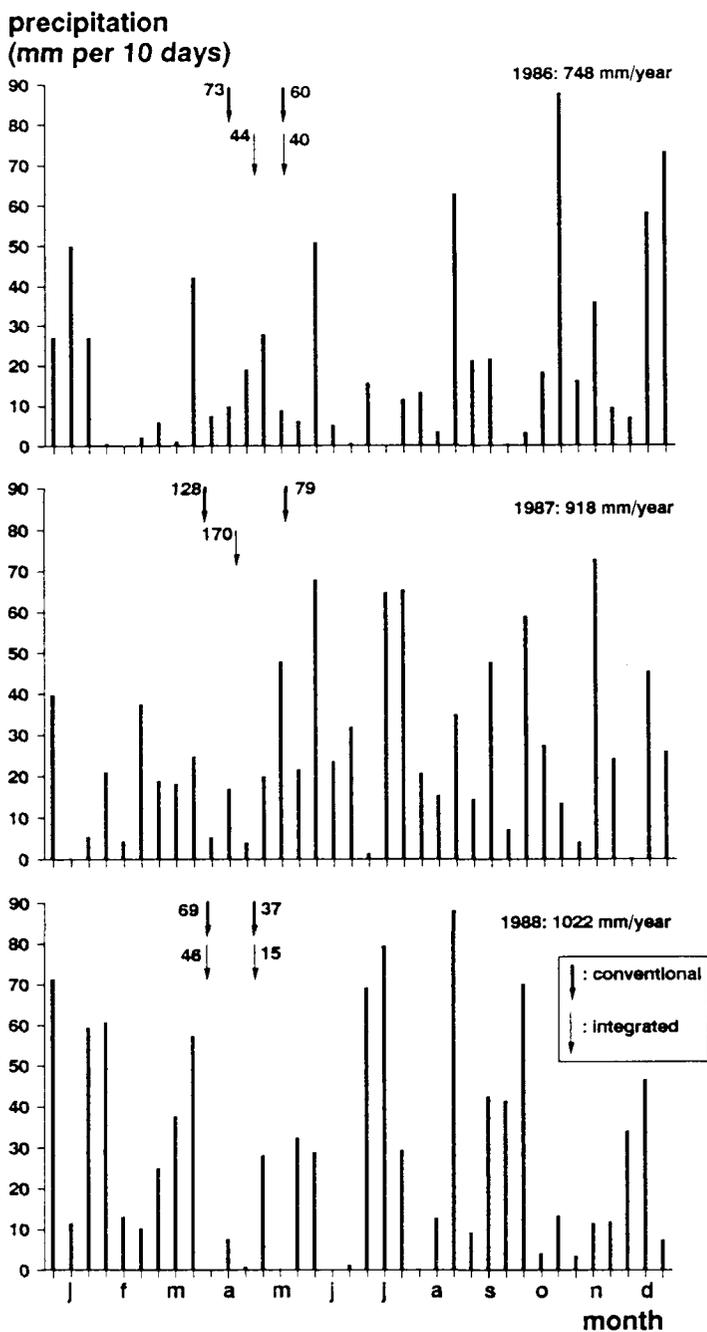


Fig. 3. Rainfall distribution during 1986-1988, with amounts of fertilizer-N or manure-N applied ( $\text{kg ha}^{-1}$ ) to fields 12B (CONV) and 16A (INT) indicated by arrows.

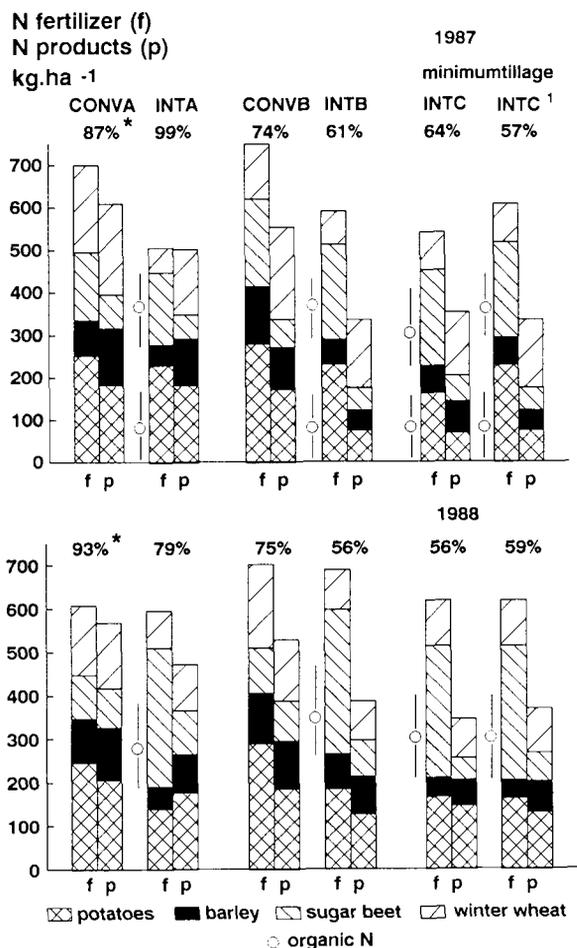


Fig. 4. Cumulative N fertilization and cumulative N removal with harvest products for the rotation in 1987 and 1988. \*  $N_p/N_f \times 100\%$ ;  $N_p$  = N in products,  $N_f$  = total-N from fertilizer and/or manure.

was largest in the case of conventional N fertilization. The lower amounts of N removed in the integrated variants were associated with lower crop yields (Table 3) and often lower N contents of the products (not shown). Yields under integrated management were acceptable compared with our aim of 80-90 % of the conventional yields on block B. The minimum tillage variant did not yet reach that aim, as might be expected, since it was already known from another field experiment at the same site that this transition needed about 10 years to give optimum yields. Yields on block A were on average higher than on block B, reflecting a long-term positive effect of the higher organic matter content on block A than on block B.

N removed in harvested products as a percentage of N applied in fertilizers and manures (input/output 'N-use efficiency') decreased as follows: CONVA  $\geq$  INTA > CONV B > INTB > INTC (Fig. 4). Variants on block A may have profited from

Table 3. Crop yields (t ha<sup>-1</sup>) in different years.

Variant <sup>1</sup>	Winter wheat (DW) <sup>2</sup>			Sugar beet (sugar)			Spring barley (DW)			Potatoes (FW) <sup>3</sup>				Mean relative yield (% of CONV B)
	86	87	88	86	87	88	86	87	88	86	87	88	89	
CONVA	7.6	6.5	6.3	13.5	9.3	11.2	6.4	4.9	4.8	48	52	55	67	104
CONVB	7.5	6.7	5.7	13.4	9.3	11.5	5.9	4.6	4.6	45	46	48	69	100
INTA	6.8	4.6	4.7	13.8	8.6	10.8	5.1	4.7	4.1	56	29	51	70	92
INTB	6.3	5.7	3.7	12.7	7.3	10.4	4.9	4.1	4.2	45	26	35	55	83
MTC	-	4.5	3.8	-	9.3	8.1	-	4.0	3.4	-	26	41	-	76
MTC <sup>4</sup>	-	5.8	3.1	-	7.6	7.0	-	2.9	3.2	-	24	43	50	70

<sup>1</sup> Variants: see Table 2.

<sup>2</sup> DW = grain dry weight.

<sup>3</sup> FW = fresh weight.

<sup>4</sup> Duplicate.

a higher N mineralization on block A than on block B, related to the higher organic N content in block A. The use of slowly mineralizable compost accounted for the lower N-use efficiencies of INT variants. Soil structure in block C, which was in a transitional stage after the introduction of minimum tillage in autumn 1986, may have promoted N losses under wet conditions and may have impeded N uptake by the crop under dry conditions more rapidly than on block B (J. A. de Vos, unpublished).

Sugar beet and potatoes, with high levels of N<sub>i</sub> fertilization may give higher N losses than cereals. The longer the period between fertilization and start of rapid crop growth and N uptake, the greater is the risk of N losses.

#### *N supply to the crop by mineralization*

Potential N-mineralization rates of soil organic-N and of manures increased almost linearly with temperature within the range 5-20 °C; this relationship was used to calculate temperature-corrected rates of N mineralization in the field. Mineralization rates calculated from 5 or 11 weeks incubation were linearly correlated ( $r > 0.9$ ,  $P < 0.01$ ) for samples from each of the fields 12B, 12C, 16A and 16B.

Potential N-mineralization rates varied with time and were on average highest in field 12 C with minimum tillage (Tables 4 and 5). Depending on the position of the crop residues, the potential N mineralization rate was highest in the 0-5, 0-10 cm or 10-25 cm layer, and always low in the 25-40 cm layer. A higher rate of N mineralization in the 0-25 cm layers of the INT fields 16A, 16B and 12C partly compensated for a lower level of N fertilization on these INT fields than on CONV field 12B. Homogenizing the soil samples and optimum aeration may have caused a more rapid N mineralization than under field conditions and may have resulted in overestimation of N mineralization in the field. An improvement may be the incubation of cores with intact soil structure, but because of spatial variability in the field a

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Table 4. Average N-mineralization rates of soil samples (mg N mineralized per kg dry soil in 5 weeks at 20 °C) taken from different fields (variants) at various depths over the years.

Layer (cm)	Year, period				
	1986 Apr.-Aug.	1987 May-Oct.	1988 May-Aug.	1987 May-Oct.	1988 May-Aug.
<i>Field (variant)<sup>1</sup></i>	<i>12B (CONVB)</i>			<i>12C (MTC)</i>	
0- 5				36	34
0- 10	4.9	9.2	7.5	20	22
10- 25	5.0	4.4	8.2	7.6	6.5
25- 40	4.1	3.5	5.5	4.8	4.2
40-100	3.2	-	-	-	-
<i>Field (variant)<sup>1</sup></i>	<i>16A (INTA)</i>			<i>16B (MTC)</i>	
0- 10	13	19	10	18	9.0
10- 25	8.1	8.0	12	6.2	12
25- 40	2.8	3.8	4.0	3.4	3.2
40-100	2.1	-	-	-	-

<sup>1</sup> Variants: see Table 2.

Table 5. Mean potential N-mineralization rates and mean N-flushes for soil samples taken on eight dates in 1987 and 1988.

<i>Field<sup>1</sup></i>	<i>Variant<sup>2</sup></i>	<i>n<sup>3</sup></i>	N-mineralization (mg N kg <sup>-1</sup> dry soil)		N-flush	Coefficients of correlation ( <i>r</i> )		
			5 weeks	11 weeks		5w/11w	5w/N-fl	11w/N-fl
12B	CONVB	24	6.6 a <sup>4</sup>	12.3 a	10.1 a	0.935	0.214	0.360
12C	MTC	24	10.4 c	20.4 b	13.8 b	0.950	0.834	0.838
16A	INTA	24	9.2 b,c	19.5 b	17.9 b	0.920	0.736	0.803
16B	INTB	24	8.4 b	17.2 b	14.2 b	0.925	0.826	0.879
<i>Layer (means of fields 12B, 12C, 16A and 16B)</i>								
0-10 cm		32	14.0 a	26.8 a	18.1 a	0.863	0.548	0.682
10-25 cm		32	8.0 b	16.9 b	15.4 b	0.918	0.555	0.605
25-40 cm		32	4.1 c	8.4 c	8.5 c	0.928	0.092	0.143
<i>Year (means of fields 12B, 12C, 16A and 16B)</i>								
1987		48	8.6	16.9	13.3	0.941	0.764	0.806
1988		48	8.6	17.8	14.6	0.934	0.692	0.780

<sup>1</sup> Means of 0-10, 10-25 cm and 25-40 cm layers.

<sup>2</sup> Variants: see Table 2.

<sup>3</sup> *n* = number of samples.

<sup>4</sup> Differences between means are significant at *P* < 0.001 when the letters following the mean value in a column are different.

large number of samples has to be used. To determine complex constraints of soil structure, moisture, oxygen, and soil organisms on N mineralization the use of intact soil cores may be indispensable. Another improvement may be to compare in-situ measurements of N mineralization (Raison et al., 1987) with laboratory incubation methods; we started such a comparison in 1990.

Potential N-mineralization rates in soil samples from the 40-100 cm layers were relatively high, probably due to the high organic matter contents of these layers as a result of their geological history. Since these peat-containing layers are not normally disturbed in the field, whereas they are homogenized for laboratory incubation of samples, we doubt whether these rates were achieved in the undisturbed field situation. Therefore, N mineralization from soil layers below 40 cm was not taken into account in our N-balance calculations; thus we perhaps underestimated N mineralization.

The solid fraction of the pig slurry mainly contained organic N, from which the equivalent of 58 kg ha<sup>-1</sup> was mineralized during 24 weeks at 20 °C. This partly accounted for the higher potential N mineralization rates of manured integrated fields (16A, 16B, 12C) compared with conventional field 12B in 1987 (Fig. 2 and Table 4).

Compost contained very little inorganic N and had a low N mineralization rate; thus it hardly contributed to the N supply of the sugar beet crops in 1988. The slow mineralization also prevented N losses during the winter '87/'88. However, applications of compost contribute substantially to the maintenance of soil organic matter and organic-N levels in integrated management.

Simulation of C and N turnover of organic matter (inputs) can be used, when rate measurements are not available, as a first estimate for rates of N mineralization (van Faassen & Smilde, 1985; van Faassen & van Dijk, 1987). In this approach, turnover of organic matter is coupled with growth and development of the microbial biomass. Preliminary work with this model has shown that different rates of N mineralization may result, depending on the organic matter inputs from the previous crop(s). Turnover of crop residues and SOM through the microbial biomass had a tendency to decrease the variation in N-mineralization rates between the years of a crop rotation (van Faassen, unpublished).

#### *Microbial biomass (N flush)*

Microbial biomass may be a sizable pool of labile N and may contribute substantially to N mineralization during incubation of soil samples. We found a significant correlation ( $P < 0.01$ ) between potential N-mineralization rates and N flushes for samples of 0-40 cm layers from the INT fields 16A, 16B, and MT field 12C; no significant correlation was found for samples from CONV field 12B. For samples from the layers 0-10 and 10-25 cm from all four fields, N mineralization and N flush were significantly correlated ( $P < 0.01$ ), but not for samples from the 25-40 cm layer (Table 5). Analysis of variance showed, besides significant effects of field (management) and layer, also significant interaction effects of year  $\times$  layer, field  $\times$  layer or year  $\times$  layer  $\times$  field. These results show that a simple relation between N mineralization and N flush, as an estimate of microbial biomass, does not always exist.

*Trends in soil organic matter and N contents*

The starting levels of SOM and total-N contents on blocks A and B showed a tendency to differentiate into four levels as a result of changes in management (Fig. 5). As expected, the high SOM content of block A could not be maintained under conventional management, but total N showed a more conservative trend than

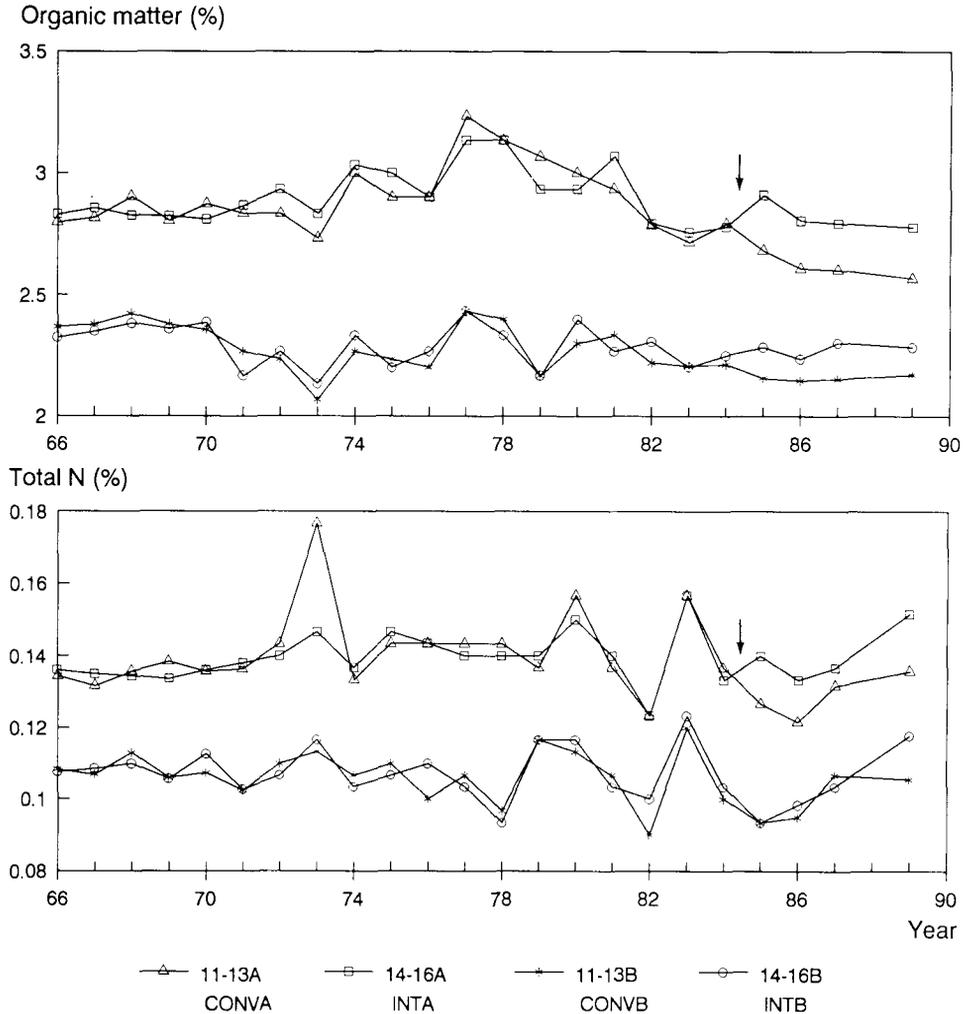


Fig. 5. Trends in soil organic matter and total-N contents in 0-25 cm layer, period 1966-1989. Each point represents the average value for three fields that have been part of the variants CONVA, CONV B, INTA and INTB since autumn 1985. Variants: see Table 2. Arrow = start of conventional and integrated management.

SOM. The low SOM content of block B also decreased slightly under conventional management, but total N was again more conservative than SOM. Integrated management, on block A as well as on block B, more or less maintained SOM content, but total N had a tendency to increase under these variants. A change in SOM and/or total-N content meant that steady-state conditions did not (yet) apply.

Equilibrium or steady-state means that net N mineralization must be compensated for by inputs of organic N from crop residues and organic manures. In the long term, steady-state conditions will determine the contribution of N mineralization to N supply of crops. Within a rotation cycle the organic-N pool will fluctuate. However, small changes in the very large pool of soil organic N cannot be quantified accurately. An absolute change in soil organic N of 0.01 % represents about 300 kg ha<sup>-1</sup> for the 0-25 cm layer (Legg & Meisinger, 1982). A more accurate, quantitative confirmation of the trends in SOM and total-N levels in Figure 5 has to await results from a longer period.

#### *N losses to the environment*

The magnitude of the N losses due to denitrification, nitrate leaching and NH<sub>3</sub> volatilization strongly depends on weather conditions and soil management. By making separate N-balance sheets over parts of the growing season, it is easier to relate N losses to the occurrence of a particular process, based on the prevailing weather and soil conditions, and on plant development during that period. Figure 6 gives an example for winter wheat in 1986. Crop N-uptake was simulated based on data from periodic harvests, and N mineralization was simulated based on potential rates measured in the laboratory, corrected for temperature. The resultant mineral-N content in soil was then calculated from Equation 1. Heavy rainfall, 50 mm within three days in June 1986, when soil nitrate levels were still high, may account for a nitrate-N loss of 60 kg ha<sup>-1</sup> in field 16A and 37 kg ha<sup>-1</sup> in field 12B, probably by denitrification (Fig. 6). However, near the end of the growing season measured N<sub>i</sub> in field 12B almost equaled the amount calculated from the N<sub>i</sub> balance, whereas for field 16A an N deficit of about 50 kg ha<sup>-1</sup> persisted. Although denitrification is a plausible explanation for the calculated deficit in the inorganic-N balance of field 16A (Fig. 2a), overestimation of N mineralization may be an alternative explanation. Further evidence to support the role of denitrification in field 16A, but not in field 12B, stems from laboratory measurements: soil cores from field 16A showed higher rates of respiration than soil cores from field 12B, and only in the cores from field 16A was denitrification found (van Faassen, unpublished).

The application of manure to field 16A in May 1987, under wet conditions, may also have promoted denitrification, because it supplied a carbon source, while the oxygen supply was limited due to soil compaction by heavy machinery. Minimum tillage may also have furthered denitrification in the MT variants, since it concentrated crop residues in the compacted 0-5 cm layer with fewer gas-filled soil pores than in the other variants.

When N mineralized from crop residues in autumn is not taken up by a green ma-

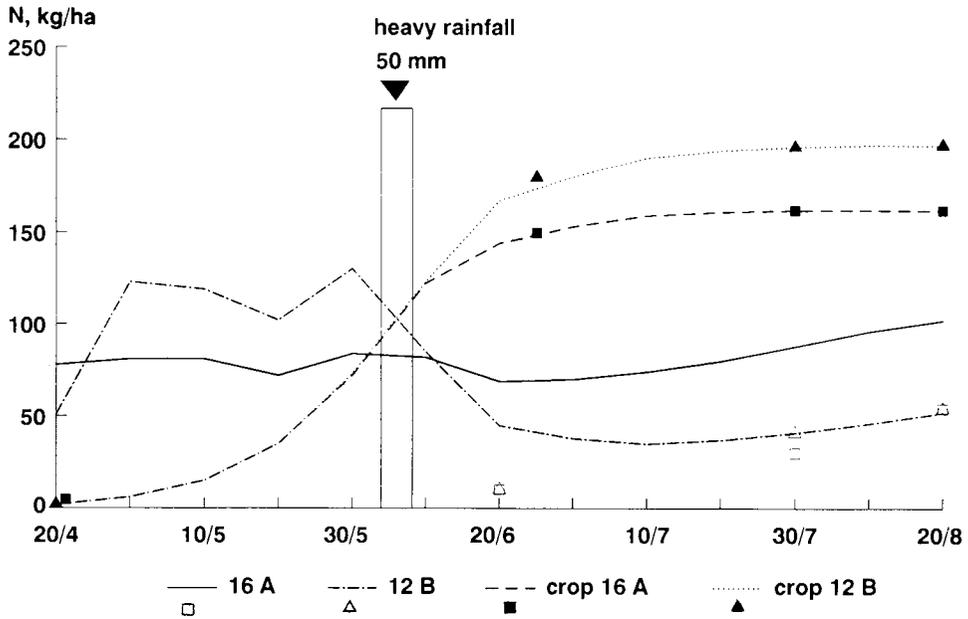


Fig. 6. Simulated N uptake (lines) by winter wheat in 1986, for CONV field 12B and INT field 16A, and simulated amount of inorganic N (N<sub>min</sub>), for field 12B and field 16A, present in the soil profile (0-100 cm layer) during the growing season based on inorganic-N balance calculations. Measured amounts (symbols) of N taken up by the crop (12B, 16A) and of mineral N in the soil profile (12B, 16A).

nure crop or immobilized in the microbial biomass after addition of organic manure, nitrate can accumulate until it is leached by surplus winter rainfall. A comparison of the amounts of nitrate-N present in the soil profile before and after winter gave a first estimate of the amounts of nitrate lost, by leaching and/or denitrification (Table 6). In November 1986, more nitrate was found in fields where potatoes had been grown, and also in deeper layers, than after cereal crops and after sugar beet. This accounts for the fact that on average more nitrate was lost during this winter from the fields where potatoes had been grown. Because of the position of

Table 6. Mean and range of nitrate-N contents (kg ha<sup>-1</sup>) in the 0-60 cm layer of the fields in November 1986 and 3 months later; rainfall during this period was 248 mm.

Crop (1986)	n <sup>1</sup>	18 Nov '86	18 Febr '87	ΔN ('N-loss')
Potatoes	7	52 (36-65)	28 (15-36)	24 (21-33)
Barley	6	27 (24-31)	23 (16-28)	4 (-1-10)
Wheat	5	26 (12-45)	21 (14-32)	5 (-4-13)
Sugar beet	5	16 (13-26)	16 ( 4-32)	0 (-4-8)

<sup>1</sup> n = number of fields.

the drains, measurements of nitrate concentrations could not be used to distinguish effects of the management systems or of the crops.

From the literature no direct measurements of the leaching of nitrate following the growth of potatoes are known to us. In a review it has been concluded that potatoes are less effective in depleting the soil of mineral N than, for instance, cereals or sugar beet (Prins et al., 1988). This may increase the risk of nitrate leaching after the growth of potatoes. In Nagele, 25 km from Marknesse in the same polder, two reduced input systems have been compared with a conventional system on a farm scale since 1979 (Vereijken, 1986). Measurements at this site revealed that nitrate concentrations in the drainage water differed little under conventional and integrated management, but depended more on crop type. The highest concentrations were found following the growth of potatoes (W. P. Wadman, unpublished). The lowest nitrate concentrations were found under biodynamic management, but since this included, among other things, 40 % grass in a 10-year rotation, it could not be directly compared with the other two systems. Measures directed to reduce nitrate leaching might also further reduce nitrate leaching under the conventional and integrated management systems.

Some  $\text{NH}_3$  may have volatilized from surface-applied manure in May 1987, since part of the manure N was present as  $\text{NH}_4\text{-N}$ . The high pH of this soil (7.6) would promote  $\text{NH}_3$  volatilization.

$\text{NH}_3$  volatilization from the crops to the atmosphere may have contributed to N loss during periods of crop senescence (Nielsen et al., 1988). For this process only indirect evidence can be derived from N balance calculations, since no direct measurements were made.

To decrease N losses to the environment, and to improve N efficiency, high concentrations of  $\text{N}_i$  should be avoided, especially in periods when losses are most likely to occur. This requires a shift to smaller amounts of fertilizer  $\text{N}_i$  and/or split applications, the use of slow-release organic-N fertilizers such as compost, and a greater contribution of soil N mineralization. Furthermore, during periods without crop N uptake, N conservation should be promoted through the use of green manures, or through application of crop residues with a high C/N ratio, which immobilize N.

## Conclusions

— During the first three of four years after a shift from conventional (high input) to integrated (reduced input) management, on a calcareous silt loam soil, large deficits were calculated for the inorganic-N balance, suggesting high N losses in both systems, especially in the wet years 1987 and 1988.

— The uncertainty about actual N losses mainly depended on the uncertainty in the calculated net N mineralization for field conditions, based on laboratory incubation of soil samples. Especially uncertain was the contribution of the layer 40-100 cm, with a rather high organic matter content, to N supply of the crops.

— The soil organic matter and total-N contents showed a tendency to differentiate from their original two levels, on blocks A and B, into four levels as a result of

changes in management. The next years will show which new steady-state levels will eventually result from integrated or conventional management.

— Correlations between N mineralization rates and biomass-N flush of soil samples were found to be situation-dependent.

— On fields with initial organic matter levels of 2.2 % and 2.7 %, crop yields under integrated management were on average 83 % and 88 %, respectively, of crop yields under conventional management.

— In the integrated system, the spring application of pig manure had to be changed to autumn application of spent mushroom compost, to prevent N loss by NH<sub>3</sub> volatilization and by denitrification. The use of compost is also needed to maintain a high level of soil organic N.

— To minimize the risk of N losses to the environment, soil inorganic N concentrations should be kept low, especially in periods when no active crop is present and N losses are most likely to occur.

### Acknowledgements

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# Biomass, composition and temporal dynamics of soil organisms of a silt loam soil under conventional and integrated management

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## Abstract

Field plots under conventional (CF) or integrated (IF) farming and cropped to winter wheat were sampled in 1986 for various soil organisms. Organisms were assembled in functional groups, based on their main food source and life-history characteristics. Total biomass of soil organisms was, on average, 690 kg C ha<sup>-1</sup> under CF and 907 kg C ha<sup>-1</sup> under IF during the growing season. Bacteria constituted more than 90 %, fungi approximately 5 %, and protozoa less than 2 % of the total biomass. Nematodes and microarthropods were less important in terms of biomass C. Carbon flow through the protozoa was estimated to be 158 and 195 kg C ha<sup>-1</sup> yr<sup>-1</sup> in CF and IF, respectively, corresponding to 20 % of the estimated bacterial production in both conventional and integrated farming. Nitrogen mineralization by the protozoa was estimated to be 30.5 and 37.6 kg N ha<sup>-1</sup> yr<sup>-1</sup> in conventional and integrated farming, respectively. Nematodes were less important than protozoa in terms of direct C and N transfer. The direct contribution from microarthropods was insignificant. Results are discussed in terms of effects of the soil biota, in particular the soil fauna, on C and N transfer in arable soil.

*Keywords:* bacteria, fungi, protozoa, nematodes, mites, collembola, biomass, carbon, nitrogen, soil, conventional management, integrated management

## Introduction

Several areas in the Netherlands are facing environmental problems due to contamination of groundwater by nitrate and pesticides, and due to deterioration of soil structure associated with the use of heavy machinery. Apart from causing environmental problems, conventional farming (CF) is associated with high costs of

agrochemicals and machinery, constituting a high energy demand. Integrated farming (IF) has been suggested as a new direction to overcome many problems associated with CF (e.g. Vereijken, 1986). In integrated farming, reduction of input in terms of inorganic fertilizers, pesticides and, in some cases, soil tillage will initially decrease crop production. However, in economic terms this might, to a greater or lesser extent, be offset by lower costs (Vereijken, 1989).

For the development of integrated farming basic knowledge on biological mechanisms in the functioning of the soil – crop ecosystem is needed (Brussaard et al., 1988). The Dutch Programme on Soil Ecology of Arable Farming Systems has the objective to obtain such knowledge with respect to matching the nutrient supply by the soil and the nutrient demand by crops, and with respect to enhancement of the contribution of soil organisms to soil structure formation (Brussaard et al., 1988). Field studies include collection of data on biomass of microorganisms (bacteria and fungi) and fauna (protozoa, nematodes, collembola, mites).

The Dutch Programme on Soil Ecology of Arable Farming Systems started in 1985 and the data presented in this paper relate to winter wheat in 1986. Soil fauna was assembled in functional groups, as related to their main food source and life-history characteristics. The objective of the present paper is to present and discuss the dynamics of functional groups, in CF and IF, expressed as biomass carbon, with emphasis on the role of the soil microfauna (protozoa, nematodes) and microarthropods (mites, collembola). Biomass, activity and dynamics of the soil microflora have been analysed by Hassink et al. (submitted).

## Materials and methods

Field research was carried out at the experimental farm 'Dr H. J. Lovinkhoeve' (Noordoostpolder, Netherlands), which was reclaimed from the sea in 1942. The soil is a calcareous marine silt loam, with a pH-KCl of 7.5, an organic matter (OM) content of 2.3-2.8 % and a total nitrogen (N) content of 0.09-0.14 %, both depending on the history of the various trial fields. The annual rainfall is 650-800 mm. Three different types of farm management are compared: CF, IF (both since 1985) and IF with minimum tillage (since 1986). The latter will not be discussed here. The site and farm management characteristics of CF and IF were described in detail by Kooistra et al. (1989).

In 1986, data were collected from winter wheat plots under conventional management and under integrated management. Conventional management was practiced on top soil with an organic matter content of 2.3 %, integrated management on top soil with an organic matter content of 2.8 %. On both plots a four-year rotation of winter wheat — sugar beet — spring barley — potatoes was started in autumn 1985, following a six-year rotation (conventional plot) or a six-year rotation plus two-year's ley (integrated plot) during 1953-1985. On both plots, winter wheat and sugar beet were cropped in 1984 and 1985, respectively. Integrated differed from conventional in reduction of N fertilizer application to 50-60 % of the recommended dosages (from 130-285 to 65-170 kg ha<sup>-1</sup> yr<sup>-1</sup>, depending on crop), in drastic reduction of pesticide applications (e.g. no soil fumigation with 1,3-

SOIL ORGANISMS UNDER CONVENTIONAL AND INTEGRATED MANAGEMENT

Table 1. Farm management at conventional (CF) and integrated (IF) farming at the Lovinkhoeve site preceding and during growth of winter wheat in 1985/1986 (after Kooistra et al., 1989).

Management	CF	IF
<i>Tillage</i>		
Autumn 1985	Plough Depth: 20 cm	Fixed-tine cultivator + lifting the soil without inversion Depth: 12 cm + 8 cm
Spring 1986 (seedbed)	Spring-tine cultivator Depth: superficial	Spring-tine cultivator Depth: superficial
<i>Fertilizer</i>		
N	200 kg ha <sup>-1</sup> <sup>a</sup>	155 kg ha <sup>-1</sup> <sup>a</sup>
<i>Crop protection</i>		
Weed control	Mainly chemical	Mainly mechanical
Pest control	Recommended dosages of pesticides (EIPRE system)	Less pesticides
	Soil fumigation with 1,3-dichloropropene after harvest	No soil fumigation

<sup>a</sup> Including the amount of soil mineral N (0-100 cm) in early spring.

dichloropropene under integrated management) and in reduction of soil tillage (20-25 cm plough in conventional, 12-15 cm plough or cultivator in integrated); see Table 1. On each sampling date (18 April, 20 June, 30 July, 19 August and 18 November 1986) samples of the top 25 cm were taken from each of three subplots (3 m<sup>2</sup>) on CF and IF, and analysed in two separate layers (0-10 and 10-25 cm). Details of the processing of samples, determination of numbers and calculation of biomass C are given below for each group of organisms considered in this paper. Physiological parameter values needed for the calculation of the contributions of faunal groups to the transfer of C and N were adopted from Hunt et al. (1987), unless stated otherwise.

*Bacteria and fungi*

Samples for estimating bacteria and fungi were taken from 10 bulked cores (diameter 2.5 cm), taken randomly in each subplot. Bacteria were counted in europium-chelate-stained soil smears using a Zeiss epifluorescence microscope (magnification × 1000) equipped with a HBO-50 mercury lamp. A 1:10 diluted soil suspension was homogenized in a blender for 30 seconds at full speed. Of the sus-

pension 10  $\mu\text{m}$  were fixed on a microscope slide and stained with europium chelate solution for 2 hours (Anderson & Westmoreland, 1971). The slides were rinsed with 50 % ethanol, air-dried and mounted with Eukitt synthetic resin.

Bacteria were grouped into two size classes: length  $<$  approximately 1  $\mu\text{m}$ , and length  $>$  1  $\mu\text{m}$ . A dry weight mass:volume ratio of 0.8 was assumed for bacterial biomass calculations and a carbon content of 40 % of the dry mass was used for calculating the total amount of carbon in the biomass (van Veen & Paul, 1979).

Fungal biomass was estimated by measurements of hyphal length and diameter using a Zeiss epifluorescence microscope (magnification  $\times$  100) equipped with a HBO-50 mercury lamp. Measurements were performed in agar films, made by mixing 1 ml of a 1:10 diluted soil suspension and 9 ml of agar, stained with fluorescent brightener No. F-6259 (Sigma, St. Louis, MD). After staining for 20 minutes the slides were rinsed with 50 % ethanol. A conversion factor of 0.33 (ratio between dry mass and wet volume) was used for biomass calculations and a carbon content of 40 % of the dry weight (van Veen & Paul, 1979).

N mineralization was determined by measuring the increase in mineral N after incubation of mixed and sieved soil samples at various temperatures for 5 weeks. Mineral N was measured after extraction with 1N KCl solution for 1 hour using a soil:water ratio of 1:2.5.

### *Protozoa*

Soil sampling was similar to that for bacteria. Protozoa were enumerated by the most probable number (MPN) method after Darbyshire et al. (1974), using two-fold dilution series in Prescott and James' (P&J) medium (Prescott & James, 1955) and *Pseudomonas fluorescens* as food bacterium. Subsamples, containing 50 g of soil, were mixed thoroughly in 500 ml P&J and subsequently diluted in microtiter plates. The number of flagellates, amoebae and ciliates originally present in soil were estimated from MPN data using a GENSTAT computer programme. The C and N contents of flagellates and amoebae were estimated from the cell numbers using the following assumptions (Band, 1959; Heal, 1971; Sinclair et al., 1981; Frey et al., 1985; Hunt et al., 1987):

- cells were spherical with diameters of 3 and 7  $\mu\text{m}$  for flagellates and amoebae, respectively;
- specific density = 1;
- dry mass = 20 % of wet mass;
- C content = 50 % of dry mass;
- C/N ratio = 7.

### *Nematodes*

Three soil samples of approximately 120 g each were taken randomly per subplot with a drill (diameter 2.5 cm) and stored in closed jars at 4 °C until nematodes were isolated, within a few weeks after sampling. Nematodes were isolated from 100 g field moist soil by elutriation (Oostenbrink, 1960), allowed to move through a nema-

tode filter in 24 hours and stored in 150 ml demineralized water at 5 °C. Nematode suspensions were homogenized by bubbling air through the water and numbers were counted in triplicate in 2 ml suspension under a stereo microscope. Sixty specimens per sample were identified to variable taxonomic levels under a high power microscope. Taxa were combined to four different feeding categories (functional groups): bacterivorous, omnivorous, fungivorous and phytophagous nematodes. Results from 9 samples per plot were averaged. The average nematode density and taxonomic composition in the plough layer (0-25 cm) was calculated from the information on the two soil layers 0-10 and 10-25 cm.

Numbers per 100 g of field moist soil were multiplied by  $3.25 \times 10^7$  for transformation to numbers per ha. Individual fresh mass of the representatives of functional groups was taken from Sohlenius & Sandor (1987). For transformation to amount of C per ha, numbers were multiplied by the specific mass of nematodes for each functional group assuming a carbon content of 10 % of the fresh mass (Jensen, 1984).

### *Microarthropods*

Soil cores (6 cm diameter and 25 cm depth; three cores on each of three subplots on IF, two on each of three subplots on CF) were taken with a metal split-corer and transferred undisturbed to the laboratory in insulated containers. Five layers of 2.5 cm per core (0-2.5, 2.5-5, 7.5-10, 15-17.5 and 22.5-25 cm) were inverted and extracted intact for 10 days using a modified MacFadyen high-gradient system (Andrén, 1985). Microarthropods were collected in picric acid, sorted, mounted in Gisin's fluid (Gisin, 1960), identified to species or family level and counted. According to the literature (Walter, 1987; Moore et al., 1988; Walter et al., 1988) and our own observations seven functional groups were defined as: fungivorous collembola, predaceous collembola, bacterivorous mites, nematophagous mites, chewing mites (mainly Oribatida), piercing mites (mainly Prostigmata) and predaceous mites. Some groups are not distinguished as such in the literature and therefore deserve explanation. *Histiostoma litorale* is an anoetid mite with enlarged membraneous palps and chelicerae which rapidly move in and out of the liquid substrate, together facilitating an almost filter-feeding mode of food intake. The species may be mainly bacterivorous (Stammer, 1959) and constitutes the functional group bacterivorous mites. *Alliphis halleri* is a mesostigmatid mite which specializes on nematodes (Sardar & Murphy, 1987). This species largely constitutes the functional group nematophagous mites. Although collembola are generally considered fungivorous, many species are known to prey on nematodes as well (Walter, 1987). *Friesea mirabilis* is exceptional among collembola in that it is considered to be mainly predaceous (Petersen, 1971). This species constitutes the functional group predaceous collembola. Under the microscope (magnification 100×) the mean length per taxon was determined, from which the dry mass was calculated (Edwards, 1967) per taxon and per functional group. The amount of carbon per ha was calculated per functional group, depth (0-10 cm and 10-25 cm) and sampling date, using a C/N ratio of 8.

## Results

The amounts of biomass C in the various functional groups on the five sampling dates are given in Figure 1, separately for CF and IF, and the layers 0-10 and 10-25 cm.

### *Bacteria and fungi*

Bacteria constituted by far the largest biomass pool. Fungi only represented approximately 5 % of the microbial biomass. Both bacterial and fungal biomass were greater in IF than in CF (Fig. 1a), which is probably related to the higher organic matter content of IF (Table 2; Schnürer et al., 1985). No consistent pattern in the depth distribution of microbial biomass was apparent on CF, whereas on most dates relatively more microbial biomass was found in the top 10 cm than in the 10-25 cm layer of IF. This is probably related to the shallow (12 cm) tillage on IF with no inversion, as a result of which crop residues remained near the surface.

The fourth sampling date (19 August) coincided with the date of harvest at the end of a dry summer period which began in mid June (Fig. 2). The drought resulted in very low moisture contents of the top soil in both plots and probably led to the low microbial biomass on 19 August (Fig. 3; Elliott et al., 1984; Schnürer et al., 1986; Granatstein et al., 1987).

Assuming a turnover rate of  $1.2 \text{ yr}^{-1}$ , the bacterial production has been  $751 \text{ kg C ha}^{-1}$  on CF and  $996 \text{ kg C ha}^{-1}$  on IF.

### *Protozoa*

At the Lovinkhoeve site the protozoan pool was  $10.5 \text{ kg C ha}^{-1}$  on CF and  $13 \text{ kg C ha}^{-1}$  on IF. In all cases amoebae had a higher biomass than flagellates (Fig. 1b). The number of ciliates was below the detection limit of the most probable number technique. There was no consistent pattern in the depth distribution on either CF or IF. Assuming steady-state, a population turnover rate of  $6 \text{ yr}^{-1}$ , and a yield of C of 40 %, the consumption of C by the protozoa in the top 25 cm was estimated to be  $158 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  on CF and  $195 \text{ kg C ha}^{-1}$  on IF. This corresponded to approximately 20 % of the bacterial production on CF and IF. Assuming a C:N ratio of bacteria of 4 and a C:N ratio of protozoa of 7, the protozoan contribution to the mineralization of N in the top 25 cm was estimated to be  $30.5$  and  $37.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in CF and IF, respectively. Fig. 4 shows the potential nitrogen mineralization rates in the 0-25 cm layer, based on laboratory incubations. The rates range between  $53$  and  $136 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  on CF and between  $113$  and  $265 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  on IF. The estimates of the protozoan contribution to nitrogen mineralization hence range between 22.5 and 57.5 % on CF and between 14 and 33 % on IF.

### *Nematodes*

At the Lovinkhoeve site the nematode pool represented approximately  $0.9 \text{ kg C}$

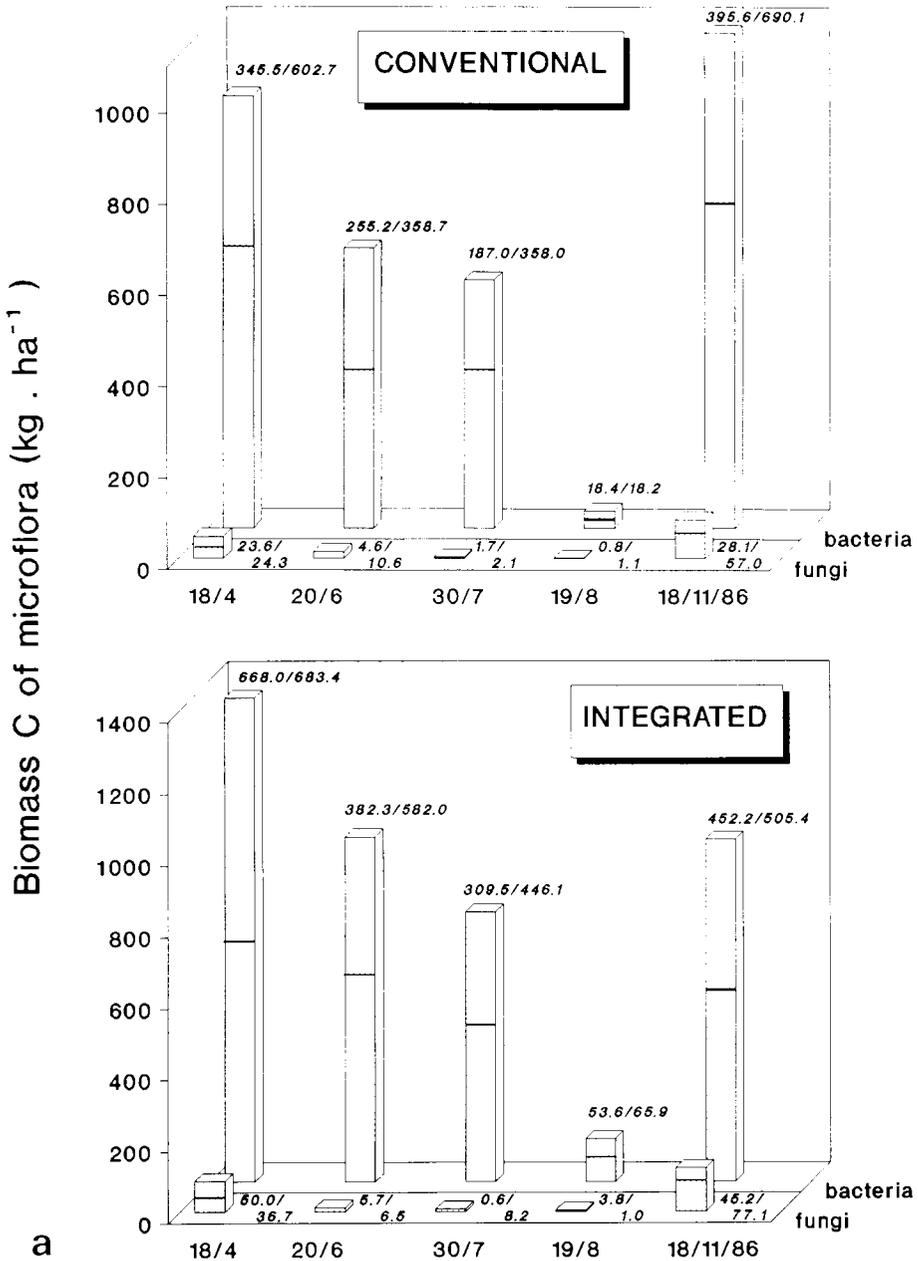


Fig. 1. Biomass C of various functional groups of soil organisms on winter wheat plots under conventional or integrated management in 1986. Figures near bars represent biomass C in the 0-10 (upper parts of bars) and 10-25 cm (lower parts of bars) layers, respectively. (a) Bacteria and fungi. Mind different scales of Y-axes.

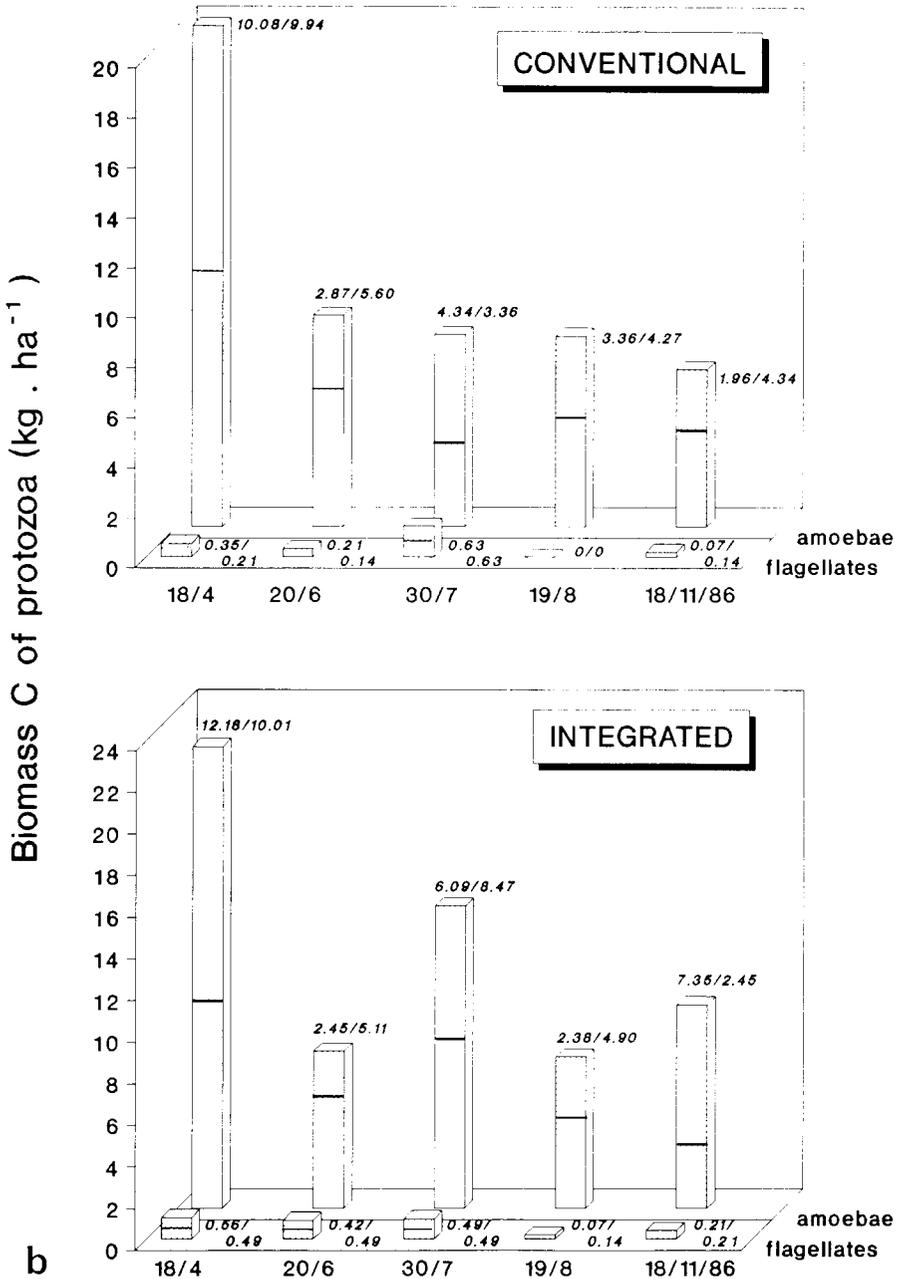


Fig. 1 continued. (b) Protozoa. Mind different scales of Y-axes.

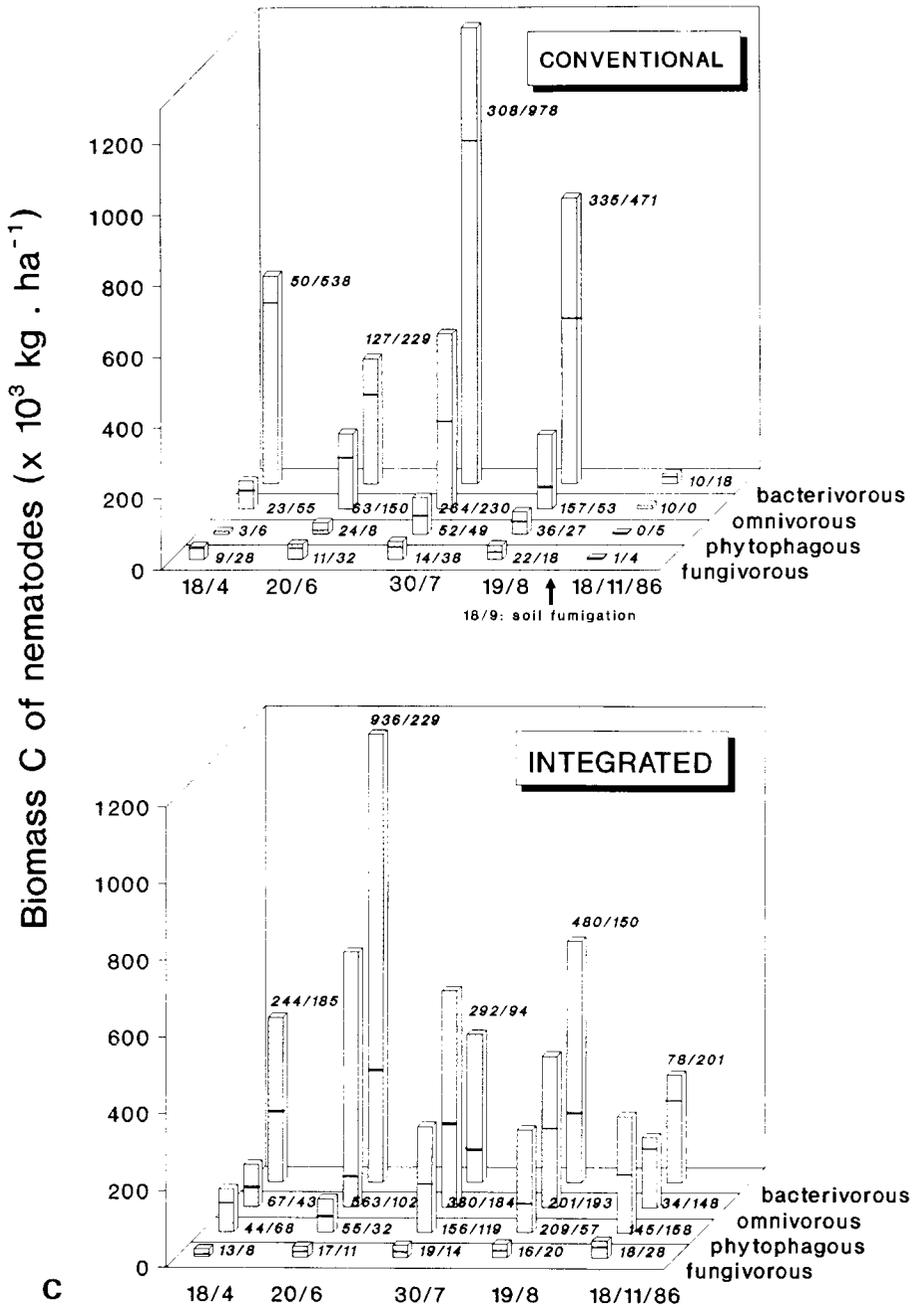


Fig. 1 continued. (c) Nematodes.

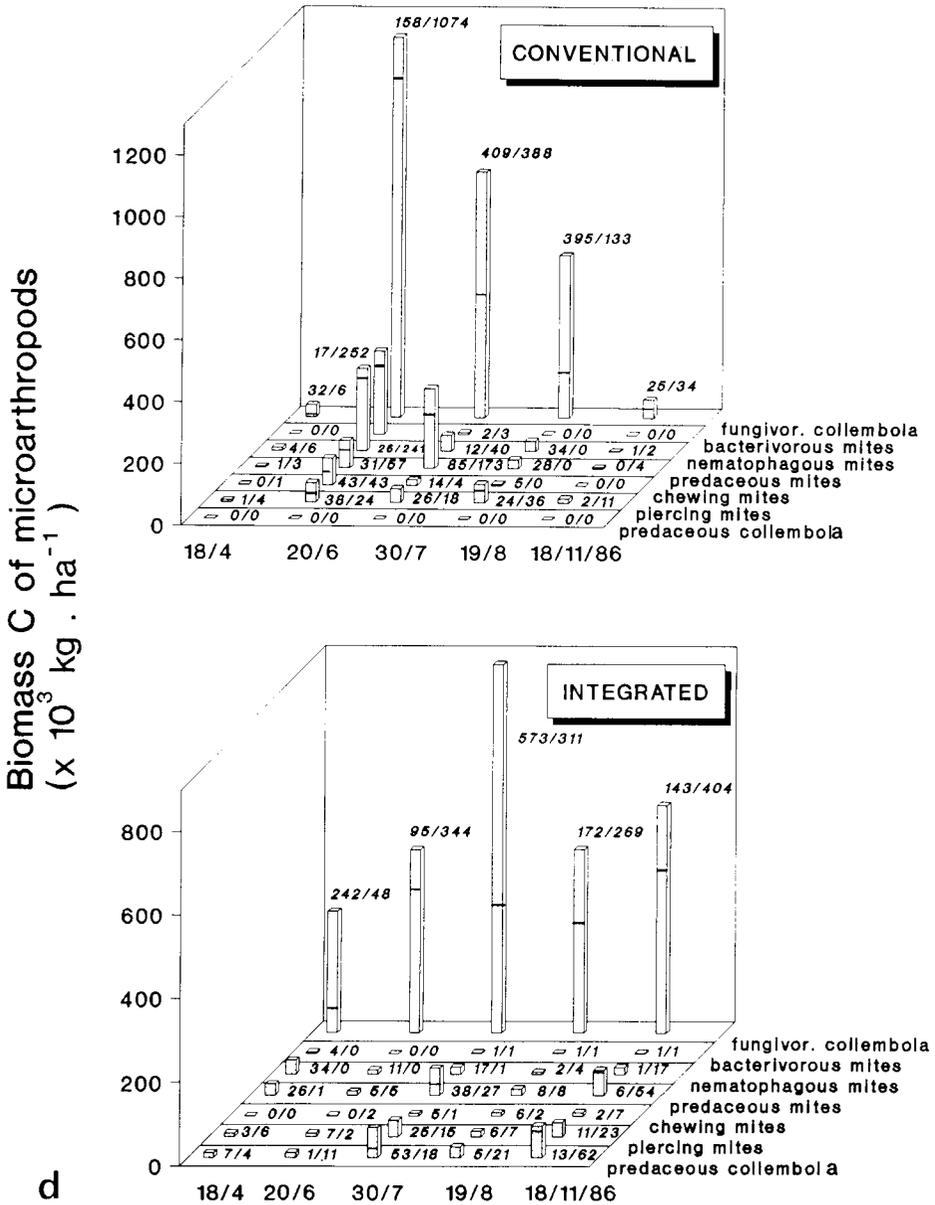


Fig. 1 continued. (d) Microarthropods. 'Chewing mites' mainly refers to Oribatida, 'piercing mites' to Prostigmata. Mind different scales of Y-axes.

SOIL ORGANISMS UNDER CONVENTIONAL AND INTEGRATED MANAGEMENT

Table 2. Organic matter content (%) and input of organic matter (kg ha<sup>-1</sup>) immediately prior to and during growth of winter wheat at the Lovinkhoeve site, at conventional (CF) and integrated (IF) farming in 1986. SDOM = stable dead organic matter.

	CF	IF
<i>Organic matter content (%)</i>		
Depth (cm): 0-10	2.09	2.67
Depth (cm): 10-25	2.12	2.81
<i>Input of organic matter (kg ha<sup>-1</sup>)</i>		
Previous crop <sup>1</sup>	500	4500
Exudation from wheat <sup>2</sup>	1940	1900
Degradation of SDOM <sup>3</sup>	1370	1750
Total	3810	8150
Total carbon (50 %)	1905	4075

<sup>1</sup> Sugar beet, input was different for CF and IF: CF obtained roots only, whereas IF also obtained leaves.

<sup>2</sup> Assumed to be 10 % of primary production (Woldendorp, 1981).

<sup>3</sup> Degradation of SDOM assumed to be 2 % per year (Kortleven, 1963); CF < IF, because of somewhat higher organic matter content in IF plots.

ha<sup>-1</sup> in CF and 1.2 kg C ha<sup>-1</sup> in IF. The nematode fauna was dominated by bacterivores and omnivores on CF, while on IF phytophagous nematodes were almost as abundant as omnivores (Fig. 1c). Because omnivorous nematodes, mainly consisting of Dorylaimida, are considered to feed largely on bacteria, bacteria were the main food source for the nematodes. There was a marked difference between CF and IF in the depth distribution of bacterivores and, to a lesser extent, fungivores, their numbers being higher in the top 10 cm in IF and in the 10-25 cm layer in CF, whereas in both CF and IF numbers of phytophagous and omnivorous nematodes were highest in the upper soil layer. The bacterivores were dominated by Rhabditidae, which are indicative of degrading fresh organic matter under moist conditions (Southey, 1982). Their depth distribution reflected the distribution of residues of the previous crop as affected by soil tillage: shallow without soil inversion under IF and ploughed down under CF (Table 1). Rhabditidae and the also bacterivorous Monhysterida showed considerable fluctuations in numbers (data not shown). The other taxa fluctuated either with a smaller amplitude (fungivores) or increased gradually in number parallel to crop development (bacterivorous Cephalobidae and Panagrolaimidae, and phytophagous nematodes). Soil fumigation in autumn wiped out the nematode fauna almost completely, irrespective of taxon.

Although differently distributed over the two soil layers sampled, bacterivores and fungivores under IF were not different in biomass from those under CF. Phytophagous nematodes (mainly *Paratylenchus* and *Rotylenchus/Helicotylenchus*) and omnivores, however, were more abundant under IF throughout the 1986 sea-

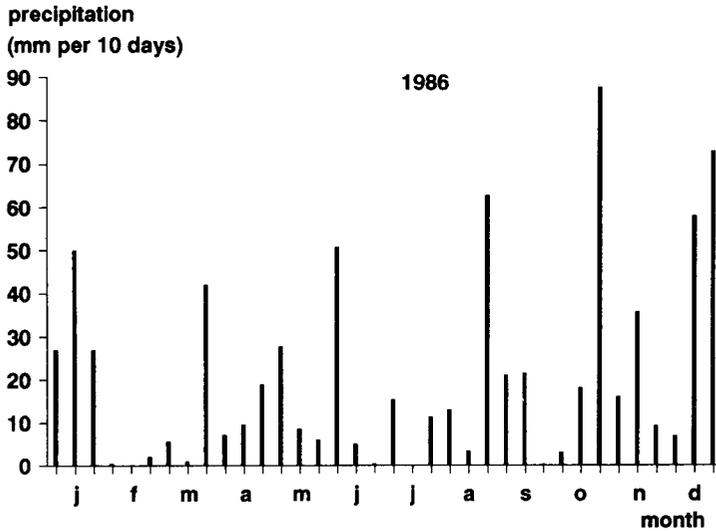


Fig. 2. Precipitation at the Lovinkhoeve experimental farm during 1986.

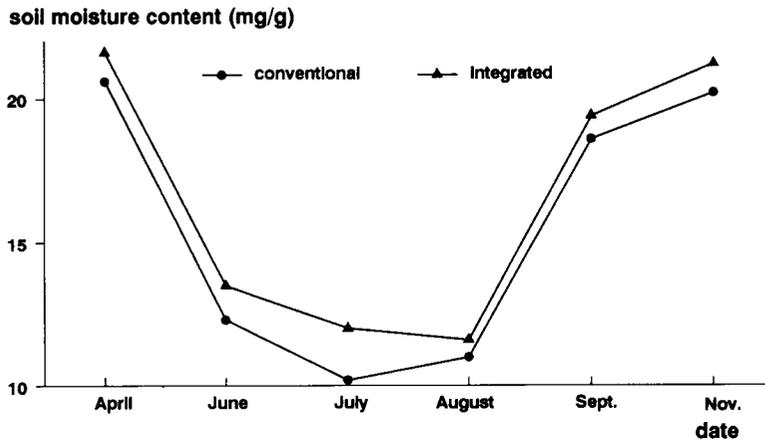


Fig. 3. Soil moisture content of the top 25 cm of the conventional and the integrated plot during 1986.

son. Assuming a population turnover rate of  $10 \text{ yr}^{-1}$  (Sohlenius et al., 1988), an assimilation efficiency of 0.6 and a production efficiency of 0.37, the consumption of C by the nematodes was estimated to be  $40.5 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  on CF and  $54.1 \text{ kg C}$  on IF in the top 25 cm, which corresponds to 5.4 % of the bacterial production on CF and IF.

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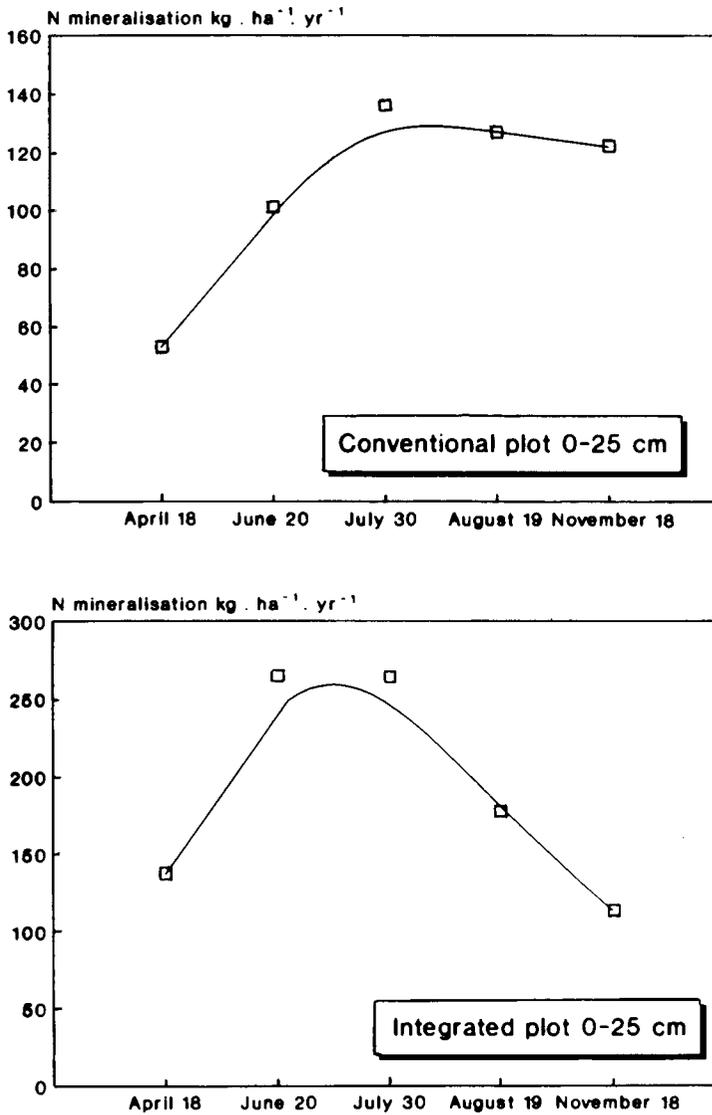


Fig. 4. Potential nitrogen mineralization rates during 1986. Mind the different scales of the Y-axes.

Assuming a C:N ratio of bacteria of 4 and a C:N ratio of nematodes of 10, the nematode contribution to the mineralization of N in the top 25 cm was estimated to be 2.0 and 2.7 kg N ha<sup>-1</sup> yr<sup>-1</sup>, respectively. The estimates of the nematode contribution to nitrogen mineralization (Fig. 4) hence range between 1.5 and 3.8 % on CF and between 1.0 and 2.4 % on IF.

*Microarthropods*

Microarthropods (mites and collembola) constituted a small fraction of the total biomass at the Lovinkhoeve site on both CF and IF. It would seem, however, that the soil fumigation in autumn on CF has had marked side-effects on the microarthropods.

Microarthropods were dominated by fungivorous collembola. They showed no consistent pattern in depth distribution, except for the nematophagous mites, which reflected the distribution of the nematodes (Fig. 1c, d). Although the differences in biomass of functional groups between CF and IF were not large, there were marked differences between the abundances of various taxa (Table 3), some of which constitute separate functional groups as mentioned in the M&M section. Based on their low biomass, generally low turnover rates and low assimilation efficiencies, the microarthropods had little direct contribution to C and N transfer on CF or IF.

Table 3. The 12 most abundant taxa of mites and collembola from the layers 0-5, 7.5-10, 15-17.5 and 22.5-25 cm below the surface of CF and IF. Sums of six soil cores (diameter 6 cm) per date per field. For numbers per m<sup>2</sup> multiply by 59.

Taxon		18 Apr	19 Jun	30 Jul	19 Aug	18 Nov	Total
Associated with CF							
<i>Hypogastrura denticulata</i>	CF	0	25	137	251	21	434
	IF	0	6	2	1	0	9
<i>Arctoseius cetratus</i>	CF	0	71	63	20	0	154
	IF	0	3	1	0	1	5
<i>Histiostoma litorale</i>	CF	4	501	59	9	0	573
	IF	24	11	23	11	21	90
<i>Folsomia candida</i>	CF	2	237	68	38	6	351
	IF	18	9	16	4	18	65
Tarsonemidae	CF	4	8	23	60	17	113
	IF	2	1	10	4	11	28
<i>Alliphis halleri</i>	CF	8	150	34	39	2	233
	IF	40	13	20	5	10	88
Pyemotidae	CF	10	144	80	196	23	453
	IF	7	20	88	34	89	238
Eupodidae	CF	1	100	55	27	3	186
	IF	5	11	52	13	21	102
Associated with IF							
<i>Onychiurus armatus</i>	CF	6	21	61	4	0	92
	IF	34	47	170	31	56	291
<i>Tullbergia krausbaueri</i>	CF	3	16	16	46	8	89
	IF	16	15	115	99	151	396
<i>T. quadrispina</i>	CF	1	0	0	0	0	1
	IF	24	2	16	19	45	106
<i>Friesea mirabilis</i>	CF	0	0	0	0	0	0
	IF	9	4	55	8	35	111

## Discussion

Our results will be briefly discussed by comparison with the literature. Subsequently, a more elaborate discussion follows on the structure and functioning of the soil ecosystem under conventional and integrated farming at the Lovinkhoeve site.

### *Comparison with the literature*

Our biomass C estimates of all groups collected at the Lovinkhoeve site were within the range published in the literature (Table 4) and our estimates of C and N transfer by the fauna agree with those published in the literature (Hendrix et al., 1986, 1987; Ingham et al., 1986; Hunt et al., 1987; Sohlenius et al., 1988; Andrén et al., 1990). Fungal biomass was low at the Lovinkhoeve site, in contrast to the Kjettslinge site (Table 4) although the methods of biomass determination used were the same. The

Table 4. Total organism biomass carbon and biomass of microfloral and faunal groups as percentages of total biomass carbon in arable soils at different sites under different management systems (n.d. = not determined).

	A		B	C	D		E		F	
	CF	IF			CT	NT	BO	B120	SM	NT
<i>Total biomass carbon</i> (kg C ha <sup>-1</sup> )	690	907	609	554	910	740	2360	3050	235	273
<i>Organisms (%)</i>										
Bacteria	93.59	91.47	75.3	47.6	76	59.5	29.7	29.5	99	99
Fungi	4.46	5.18			16.5	21.5	63.6	68.9		
Protozoa	1.52	1.43	24.6	52.3	5.5	5.4	5.9	1.0	0.6	0.6
Nematodes	0.13	0.13	0.01	0.00	0.22	0.14	0.05	0.03	0.3	0.3
Microarthropods	0.11	0.07	0.06	0.03	0.08	0.27	0.02	0.01	0.06	0.09
Macroarthropods	0.04	0.00	n.d.	n.d.	0.01	0.03	0.05	0.01	n.d.	n.d.
Enchytraeids	0.11	0.06	n.d.	n.d.	0.03	0.07	0.18	0.12	n.d.	n.d.
Earthworms	0.00	1.65	n.d.	n.d.	2.2	13.5	0.47	0.45	n.d.	n.d.

A. Lovinkhoeve site, The Netherlands, Typic Fluvaquent, silt loam, 0-25 cm, spring/summer, winter wheat.

B. Ellerslie, Alberta, Canada, Black Chernozem, silt clay loam, 0-10 cm, barley, summer/autumn (Rutherford & Juma, 1989).

C. Breton, Alberta, Canada, Gray Luvisol, silt loam, 0-10 cm, barley, summer/autumn (Rutherford & Juma, 1989).

D. Horse Shoe Bend site, Athens, Georgia, USA, Hiwassi loam, Typic Rhodudult, sandy clay loam, 0-15 cm, winter/spring, grain/rye (Hendrix et al., 1986; 1987).

E. Kjettslinge site, Sweden, mixed, frigid Haplaquoll, loam, 0-27 cm, barley, 1982-1983 (Andrén et al., 1988; Andrén et al., 1990).

F. Akron, Colorado, USA, Mollisol, 0-10 cm, fallow/wheat, summer (Elliott et al., 1984).

CF = conventional management, IF = integrated management, CT = conventional tillage, NT = no tillage, BO = no N-fertilizer, B120 = 120 kg N fertilizer ha<sup>-1</sup>, SM = stubble mulch.

low biomass of fungivores at the Lovinkhoeve site (Fig. 1) is consistent with the low biomass of fungi. Although it is generally assumed that microorganisms disperse well, this may not hold for many fungi (cf. Christensen, 1989) and the low fungal biomass may reflect the recent reclamation of the Lovinkhoeve site (1942) from the sea. The rather high pH of the soil (pH-KCl 7.5) is not conducive to a high fungal biomass, either. Hendrix et al. (1986, 1987) hypothesized that changing from conventional tillage to no-tillage would result in a relatively higher biomass of fungi and fungivorous animals. Data from both the Lovinkhoeve and the Horse Shoe Bend sites, however, so far indicate that bacteria remain to be the most important decomposers under various types of soil management. Amoebae were higher in biomass than flagellates which was also found in Sweden by Clarholm (1989).

### *Structure of the soil ecosystem in CF and IF*

In this study, integrated farming (IF) differed in three important aspects from conventional farming (CF) and the results will be discussed in the context of those differences:

1. The IF plot had a higher *organic matter content* and received more *crop residues* than the CF plot. The higher bacterial and fungal biomass on IF reflects these differences.
2. The relatively higher amount of microbial biomass in the top 10 cm than in the 10-25 cm layer on IF is associated with the shallow, non-inversion *tillage* on IF, which kept crop residues in the top layer. The absence of such a difference on CF is associated with the more even distribution of crop residues in the top 25 cm by ploughing. The higher biomass of bacterivorous nematodes in the top 10 cm on IF, as compared with the 10-25 cm layer, is consistent with the depth distribution of the bacterial biomass on IF. Although no clear pattern in the depth distribution of the bacterial biomass on CF was apparent, the higher biomass of bacterivorous nematodes in the 10-25 cm layer on CF, as compared with the top 10 cm, is not at variance with the soil tillage (ploughing down of crop residues) on CF. The depth distribution of nematophagous mites is consistent with that of the most abundant nematodes, the bacterivores.
3. Considerably less *pesticides* were applied on IF than on CF, the most important difference being the omission of soil fumigation on IF. Soil fumigation on CF was directed against phytophagous nematodes, in particular potato cyst nematodes. This treatment, however, also wiped out other nematode groups and may have been among the causes by which microarthropods were decreased on the last sampling date on CF. Phytophagous nematodes were, however, lower in biomass on CF than on IF throughout the season and not only following soil fumigation. This may relate to a long-term effect of soil fumigation. Phytophagous nematodes have relatively long generation times and will hence recover more slowly from soil disinfestations than other nematodes.

The organisms of most of the functional groups were not identified to the genus or species level. In the few cases where this was done, however (microarthropods), marked qualitative and quantitative differences between the fauna on CF and IF be-

came apparent (Table 3). Statistical analysis of the biomass dynamics of functional groups of the microflora, defined according to their ability to decompose a range of chemicals, showed that the characteristics of the microfloral populations changed considerably in time in both CF and IF, the differences within plots generally being greater than between plots (Hassink et al., submitted). Taking bacteria and fungi as two functional groups, Moore et al. (1990) designed food webs of CF and IF plots on the basis of the functional groups defined in this paper and they statistically analysed the food webs to identify patterns in the way species interact. The food web in CF differs from that in IF by the absence of predaceous collembola and by the near non-existence of the phytophagous nematodes. The analysis showed that the webs can be compartmented into a bacterial and a fungal channel, the degree of compartmentalisation depending on farm management: under integrated management consumers of fungi were separated in time from consumers of bacteria, as were fungi and bacteria themselves, whereas little separation was observed under conventional management (Moore et al., 1990).

Hence, the available evidence indicates that the structure of the soil ecosystem shows considerable differences between CF and IF, both in depth and in time. These differences are associated with the main differences in management.

#### *Functioning of the soil ecosystem under CF and IF*

At first sight, despite the differences in structure of the soil ecosystems under CF and IF, there seems to be remarkable similarity in their functioning. The ratio CF:IF for organic matter content, bacterial biomass, protozoan biomass and bacterivorous plus omnivorous nematodes in the 0-25 cm layer was approximately 0.8 in all cases; the estimated protozoan consumption of C corresponded to 20 % of the estimated bacterial production in both CF and IF; the estimated nematode consumption of C corresponded to 5.4 % of the estimated bacterial production in both CF and IF. Based on our estimates of the faunal contribution to the C and N transfer, protozoa were quantitatively important as were, to a lesser extent, nematodes. Yet, the validity of estimates made by us and others of the contribution of the soil biota to the transfer of C and N, although based on the best available knowledge, may be limited by various factors:

1. The steady-state assumption. Calculations of rates of C and N transfer are based on average biomass of functional groups. The biomass, however, is fluctuating (Fig. 1) and so are the transfer rates of C and N by various groups of soil organisms. The timing of mineralization is crucial for the improvement of the nutrient use efficiency and more realistic modelling of transfer rates, and comparison between CF and IF is needed.

2. Not only *when* nutrients become available (synchronization of supply by the soil and demand by the plant) but also *where* they become available is important (synchronization of supply by the soil and rooting by the plant). Simulation modelling has shown that disproportionately more material flow occurred in the upper 10 cm than in the 10-25 cm layer in IF, whereas no such difference occurred in CF (Moore et al., 1990).

3. The reliability of physiological parameters. Because assessment of physiological parameters is tedious, we relied on published values, e.g. those listed by Hunt et al. (1987). To mention only one example, turnover rates of populations are in fact nominal death rates, i.e. the inverses of the mean life spans of organisms dying because of physiological ageing. This may be realistic for protozoa, but not for nematodes and most of the other functional groups because predators contribute considerably to their death rates. For nematodes, turnover rates and, thereby, their contribution to C and N transfer, may be four times higher than assumed hitherto, because nematophagous fungi are an important death factor (Bouwman, unpublished results). Moreover, and perhaps more important in terms of comparing CF and IF, turnover rates of a functional group may be different under different management systems, e.g. depending on the quality of the added organic materials.

4. Indirect effects of the soil fauna. Indirect effects include faunal stimulation of the microflora by comminution of organic residues and enhancing the specific metabolic activity of microbial cells that escape grazing by microbivores. Evidence of such effects has been reviewed by e.g. Seastedt (1984), Moore et al. (1988), Verhoef & Brussaard (1990), and Zwart & Brussaard (1990). Indirect contributions of the fauna to C and N transfer are calculated as part of the contribution of the microflora. If such indirect effects are quantitatively important, the contribution of the fauna to C and N transfer is underestimated. Interpretation of indirect effects is, however, hampered by a lack of causal insight in the mechanisms involved. Such insight is needed to appropriately fit saproverous animals such as enchytraeids, earthworms and various macroarthropods (Table 4) into current detritus-based food webs.

To conclude, the structure of the soil ecosystem and, given the right level of observation, the functioning of the soil ecosystem differed between CF and IF as related to the different management practices. To the extent that our knowledge of the structure and functioning of agro-ecosystems increases, our understanding will increase on how to manage the soil biota towards a higher efficiency in integrated farming, i.e. to let the soil work for us *sensu* Elliott & Coleman (1988). The above-mentioned limitations to our understanding and, hence, to our management skills, have defined the scope of our current research.

### Acknowledgements

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# **Statistical analysis and simulation modelling of the belowground food webs of two winter wheat management practices**

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## **Abstract**

Soil food webs from conventional and integrated management practices at the Lovinkhoeve experimental site (Noordoostpolder, Netherlands) were analysed using multivariate statistical procedures and simulation modelling, so as to identify patterns in species interactions and material transfers.

Cluster analysis, canonical discriminant analysis and canonical correspondence analysis of the dynamics of biomass-N of functional groups within the food webs indicated that the webs could be compartmented into categories of functional groups based on food choice and trophic level. The degree of compartmentalization depended on management practice. Consumers of fungi were separated in time from consumers of bacteria under the integrated management practice whereas little separation was observed under conventional practice.

Simulation modelling was used to estimate the flux rates of nitrogen among functional groups within the food webs. The modelling demonstrated that more flow occurred in the integrated plot than in the conventional plot. More material flow occurred in the upper 10 cm of the integrated plot than in the 10-25 cm layer, whereas there was no such difference in the conventional plot. This effect may be due to the differences in the tillage practice on each plot.

*Keywords:* food webs, cluster analysis, canonical discriminant analysis, canonical correspondence analysis, nitrogen flux rates

## **Introduction**

The soils of the Noordoostpolder, Netherlands, were reclaimed from the former Zuiderzee between 1936 and 1942, and subsequently developed for agriculture. In 1953 the Lovinkhoeve experimental farm was established and since 1964 the soils

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have been under continuous cultivation with six- and four-year crop rotations that included winter wheat, sugar beets, barley and potatoes. The food webs from the Lovinkhoeve presented here are from the winter wheat rotations under a low-input integrated management practice and a high-input conventional management practice (Brussaard et al., 1988).

The architectures of the two food webs are similar in all respects except for the absence of predatory collembola in the conventional plot. The food web presented in Figure 1 (integrated practice) was drawn in a similar fashion as the food web described by Hunt et al. (1987) for the North American Shortgrass Steppe. The food web consists of five trophic positions (I-V, bottom of Fig. 1):

Position I — detritus and primary production,

Position II — primary decomposers and herbivores, i.e., bacteria, fungi (saprophytic), phytophagous nematodes,

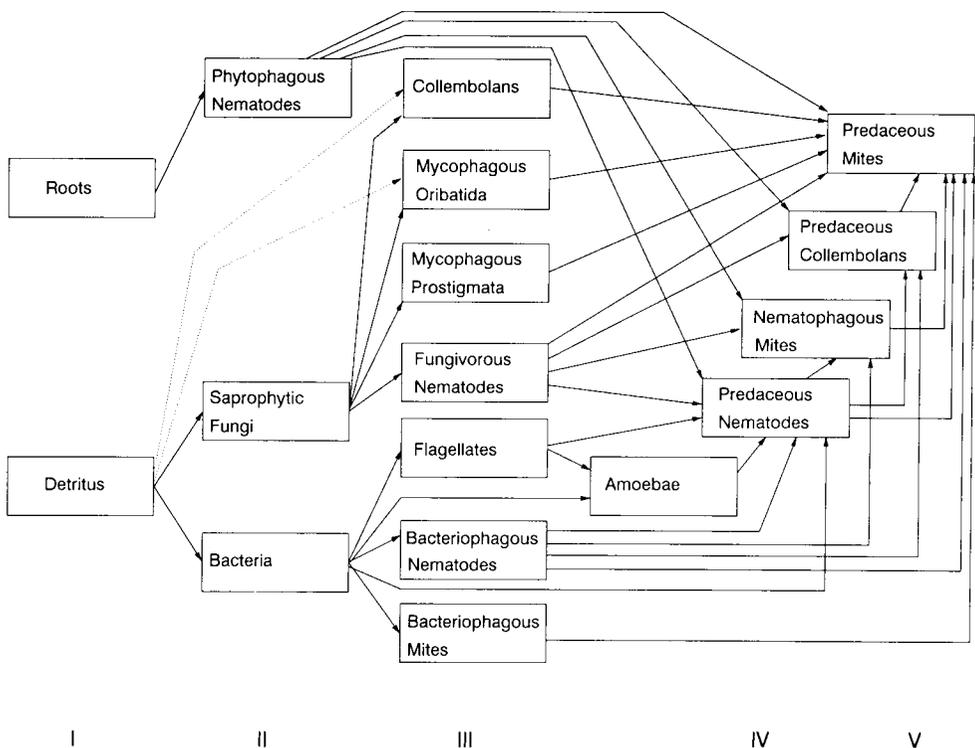


Fig. 1. Connectedness diagrams of the soil food webs of the Lovinkhoeve Experimental Farm, Marknesse, Netherlands (winter wheat). The food web presented is from the integrated plot. The food web from the conventional plot is similar to that from the integrated plot, except that predatory collembola are not present in the conventional plot. The dashed arrows indicate unquantified, potential feeding relationships. The 'Mycophagous Oribatida' represent mites that chew fungal hyphae with chelate mouthparts and 'Mycophagous Prostigmata' represent mites that pierce fungal hyphae with their mouthparts; these two groups also include some other groups than Oribatida or Prostigmata, respectively.

Position III — consumers of bacteria and fungi, e.g., collembola, mycophagous mites and nematodes, protozoa and bacteriophagous nematodes,

Position IV — intermediate predators, i.e., predaceous nematodes and nematophagous mites,

Position V — top predators, i.e., predaceous mites and collembola.

The food webs do not include some potentially important functional groups of which no field data were available, such as algae, root pathogens, annelids, mycophagous protozoa and nematophagous fungi. An analysis of the dynamics of the biomass of the individual functional groups is presented by Brussaard et al. (1990). In the present paper we use multivariate statistical analysis and simulation modelling to find patterns in the way functional groups interact and matter is transferred within the food webs. Three statistical methods were applied to the biomass data:

(1) cluster analysis (Sokal & Michener, 1959) was used to find out which functional groups show approximately similar dynamics,

(2) canonical discriminant analysis (Hotelling, 1936) was applied to categories of functional groups, based on energy source and trophic position, in order to test whether these categories differ significantly with respect to their biomass dynamics,

(3) canonical correspondence analysis (ter Braak, 1986) was used to identify and visualize the relations between seasons and biomass.

Simulation modelling (after Hunt et al., 1987, and O' Neill, 1969) was used to estimate the flows of nitrogen among functional groups. The estimates of the flows of nitrogen were used to study the dynamics of nitrogen flows originating from the different energy sources within the food webs: roots, bacteria and fungi.

## Materials and methods

### *Site description*

The soil of the Lovinkhoeve is a calcareous silt loam with pH-KCl 7.5. Annual precipitation at the site is between 650-800 mm. The results presented in this paper are from two management practices — integrated and conventional. Integrated management differs from the conventional practice mainly in reduction of N-fertilizer application to 50-65 % of the recommended dosages in the conventional practice (from 130-285 to 65-170 kg ha<sup>-1</sup> yr<sup>-1</sup>, depending on crop), a reduction of pesticide application and a reduction of soil tillage (20-25 cm plough in conventional, 12-15 cultivator or plough in integrated). In addition to these differences, the upper 20 cm of soil of the conventional plot has an organic matter content of 2.3 %, whereas that of the integrated management plot is 2.8 %. For further details, see Kooistra et al. (1989).

Prior to 1985, the conventional and integrated plots had different crop rotations. The conventional plots were under a six-year rotation, whereas the integrated plots were under a six-year rotation with two-year's ley. During the 1984 and 1985 growing seasons, both plots were under winter wheat and sugar beets, respectively. Since 1985, both plots have been under the same four-year crop rotation of winter wheat,

sugar beets, barley and potatoes. The data presented here are from the 1986 winter wheat crop.

### *Statistical methods and simulation modelling*

Cluster analysis (Sokal & Michener, 1959; Gower & Ross, 1969) was used to form clusters of functional groups that showed similar dynamics in biomass-N. The biomass-N of each functional group within the Lovinkhoeve food webs was estimated on 5 sampling dates (methods: Brussaard et al., 1990). The data were standardized by dividing the biomass-N estimate of a functional group on a given date by the sum of the total biomass-N estimates for that functional group over all five sampling dates. These standardized biomass-N estimates for each functional group were used as input for the cluster analysis. With this technique, all the functional groups were initially considered to be unique clusters and then combined to form aggregate clusters in a step-wise fashion. At each step, the two clusters with the closest Euclidean distance are merged to form a new cluster. Separation between clusters is based on an arbitrary distance  $\delta$ : the distance between each pair of groups in a cluster is less than or equal to  $\delta$ , whereas the distances between clusters are greater than  $\delta$ . Therefore, the results of a cluster analysis depend on the choice of  $\delta$ , on the distance measure (e.g. Euclidean, City Block), and on the choice of the method for merging clusters. We used two methods for merging clusters: the average link method as developed by Sokal & Michener (1959) and the single link method (Gower & Ross, 1969). Both methods resulted in the same set of clusters, which is an indication of a rather strong cluster structure.

A canonical discriminant analysis (CDA, Hotelling, 1936) was used to visualize and test the differences between the collections of functional groups, classified into one of six categories according to energy source and trophic position (Fig. 1). Bacteria, fungi and root-feeding nematodes (trophic position II) were left as separate categories. Consumers of bacteria that occupy trophic position III were grouped as bacterial feeders, and consumers of fungi that occupy trophic position III were grouped as fungal feeders. Functional groups that occupy trophic positions IV and V, and obtain their energy from consumers of roots, bacteria and fungi, were grouped as predators. The standardized biomass estimates used in the cluster analysis were used as input for the CDA. With the CDA, canonical variables (linear combinations of the proportions of biomass for each date) were determined that best summarized differences among the six categories of functional groups. After computing the canonical variables, a multivariate analysis of variance (MANOVA, test-statistic Wilk's Lambda) was conducted to determine whether the six categories showed statistically significant differences. If the MANOVA was significant ( $P < 0.05$ ), Hotelling's  $T^2$  (Hotelling, 1936) was computed from the pairwise Mahalanobis distances between pairs of categories of functional groups to determine significant differences in dynamics. Hotelling's  $T^2$  can be regarded as the multivariate extension of the univariate Student's  $t$  test for the differences of means of two populations.

Canonical correspondence analysis (CCA, ter Braak, 1986) was used to identify

and visualize the relations between sampling dates and the biomass-N of the functional groups. Canonical correspondence analysis relates species to explanatory variables, e.g., humidity, soil temperature and organic matter content under the assumption that these relationships are unimodal (ter Braak, 1986). CCA is a multivariate extension of weighted averaging and can generate biplots of species scores (in our case, scores of functional groups) on axes that are linear combinations of the set of explanatory variables provided. For the sake of comparison with the canonical discriminant analysis and the cluster analysis, we restricted the analysis to sampling date as the single explanatory variable in order to examine whether the observed patterns can be explained by contrasts between seasons.

A simulation model was used to estimate the rates at which biomass/energy is transferred among functional groups. The model can be run either as a C or an N model. We chose to run it as an N model and used the biomass-N estimates of the functional groups as input for the model. The nitrogen flux rates were calculated as follows. Assuming that the functional groups are at steady state, production must balance loss of material ( $M$ ) due to natural death and predation. The feeding rate ( $F$ ) by one functional group can be calculated (Hunt et al., 1987):

$$F = \frac{M}{Ae \times Pe}$$

where  $Ae$  is the fraction of consumption being assimilated and  $Pe$  the fraction of assimilated energy allocated to production. If dynamics are to be included, the decrease or increase in biomass of the predator ( $dE/dt$ ) has to be added to the material losses (O'Neill, 1969):

$$F = \frac{M + dE/dt}{Ae \times Pe}$$

If predators feed on more than one prey type, then both the preference of the predator for a given prey and the relative abundance of the prey in the predator's diet have to be considered. The consumption rate of the  $i$ 'th prey ( $f_i$ ) can then be calculated (O'Neill, 1969):

$$f_i = \frac{W_i \times e_i \times F}{\sum W_i \times e_i}$$

where  $W_i$  is the preference factor for the  $i$ 'th prey and  $e_i$  the density of the  $i$ 'th prey. The calculations started with flux rates between top predators and their prey, since for those predators only the mortality caused by natural death needs to be known. All flux rates could then be calculated back throughout the food web ending with those from bacteria, fungi and roots. Apart from the biomass-N data, the model requires information on the diets, feeding preferences, C/N ratios, production and assimilation efficiencies, and birth and death rates of the functional groups. We assumed that the parameters used for the shortgrass food web calculations (for references see Hunt et al., 1987) are not specific for a particular environment. Therefore, we used the same set of parameters, except for the death rates of the nematodes which were observed to be higher (approximately seven times) in

Lovinkhoeve soil (L. A. Bouwman, pers. comm.). These high death rates are caused by nematophagous fungi, which are not included in the food web description.

Before presenting the results, a word of caution is in order. Since the replication at the Lovinkhoeve was nested within the plots, and the history of the plots was different for each management practice, we did not have true replications of the food web as a whole and the management practice is confounded with plot history. The functional groups within the categories, as used in the CDA and CCA, represent replications, which may not be appropriate. Therefore, the analyses presented here constitute a case study and any reference to the results should reflect this.

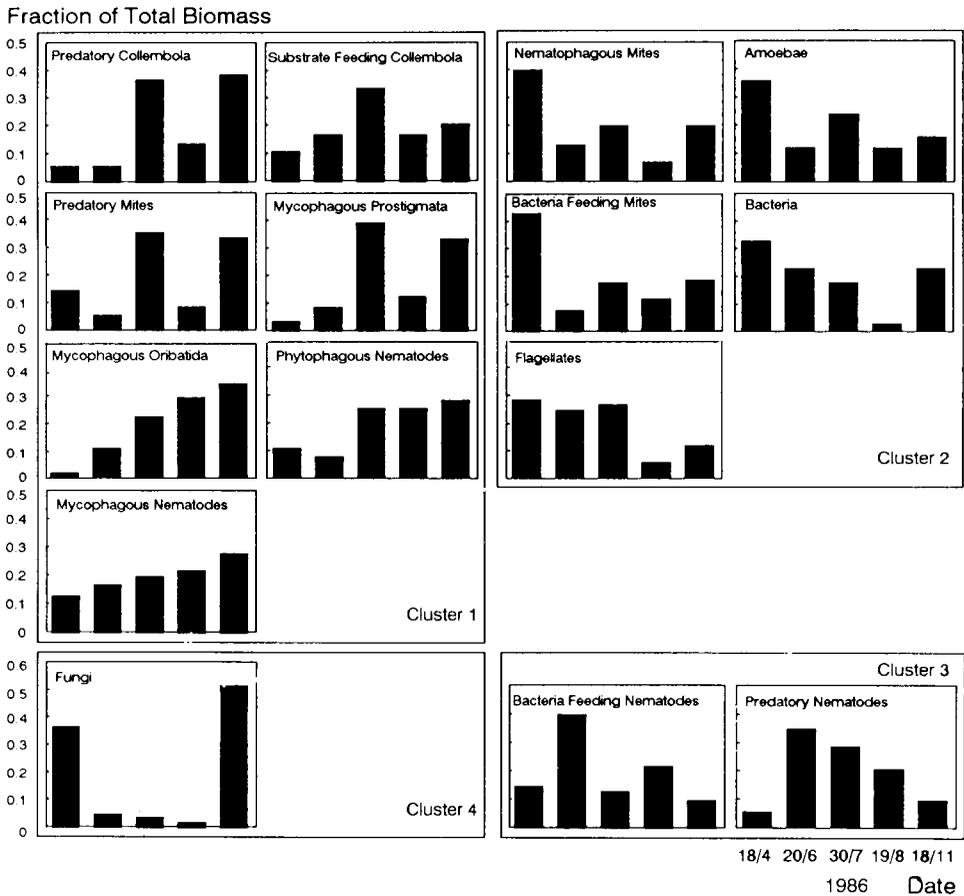


Fig. 2. Bar graphs of the fraction of total biomass-N collected over the five sampling dates for each functional group, within the integrated plot.

## Results

### *Cluster analysis*

The cluster analysis indicated that there were three clusters in the conventional plot and four in the integrated plot. For the integrated plot, the dynamics of the functional groups in each cluster are presented in Figure 2 and the dendrograms for both plots are presented in Figure 3. For the conventional plot, fungi, bacteria and amoebae separated from the other functional groups, with no apparent pattern in the memberships of the remaining two clusters. For the integrated plot, fungi separated from all other functional groups. The remaining clusters contained either fungal feeders and predators (Cluster 1) or bacteria, bacterial feeders and predators (Cluster 2 and 3). In conclusion, the cluster analysis suggested that the dynamics of functional groups in the integrated plot was dependent on the types of food they consumed. This relationship did not hold in the conventional plot, in that the bacteria and fungi were exhibiting similar dynamics but distinct from most of their consumers.

### *Canonical discriminant analysis*

Biplots of the first and second canonical variables for the integrated and conventional plot illustrate the patterns found in the cluster analysis (Fig. 4a,b): in the integrated plot, consumers of bacteria and fungi exhibited different dynamics, whereas the predators showed dynamics common to both consumer groups. In the

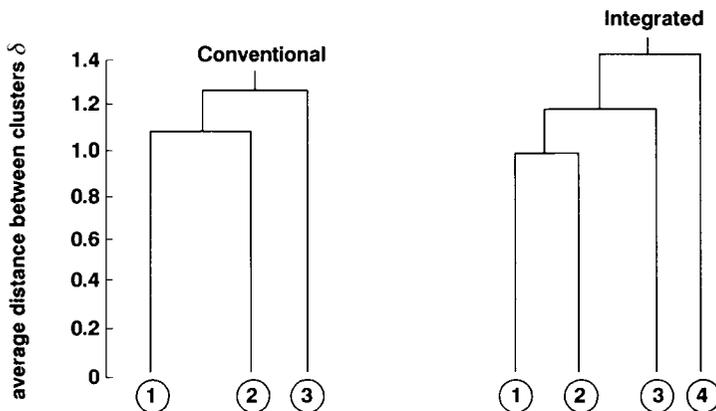


Fig. 3. Average-linkage dendrogram for distances between proportions of biomass-N on the sampling dates for the functional groups in the conventional and integrated plots. For the conventional plot, the functional groups within each cluster are: Cluster No 1 — bacteria, fungi, amoebae; Cluster No 2 — bacteriophagous mites, mycophagous oribatida, nematophagous mites; Cluster No 3 — collembola, mycophagous prostigmata, phytophagous nematodes, predatory nematodes, bacteriophagous nematodes, fungivorous nematodes, predatory mites, flagellates. For the integrated plot, see Fig. 2.

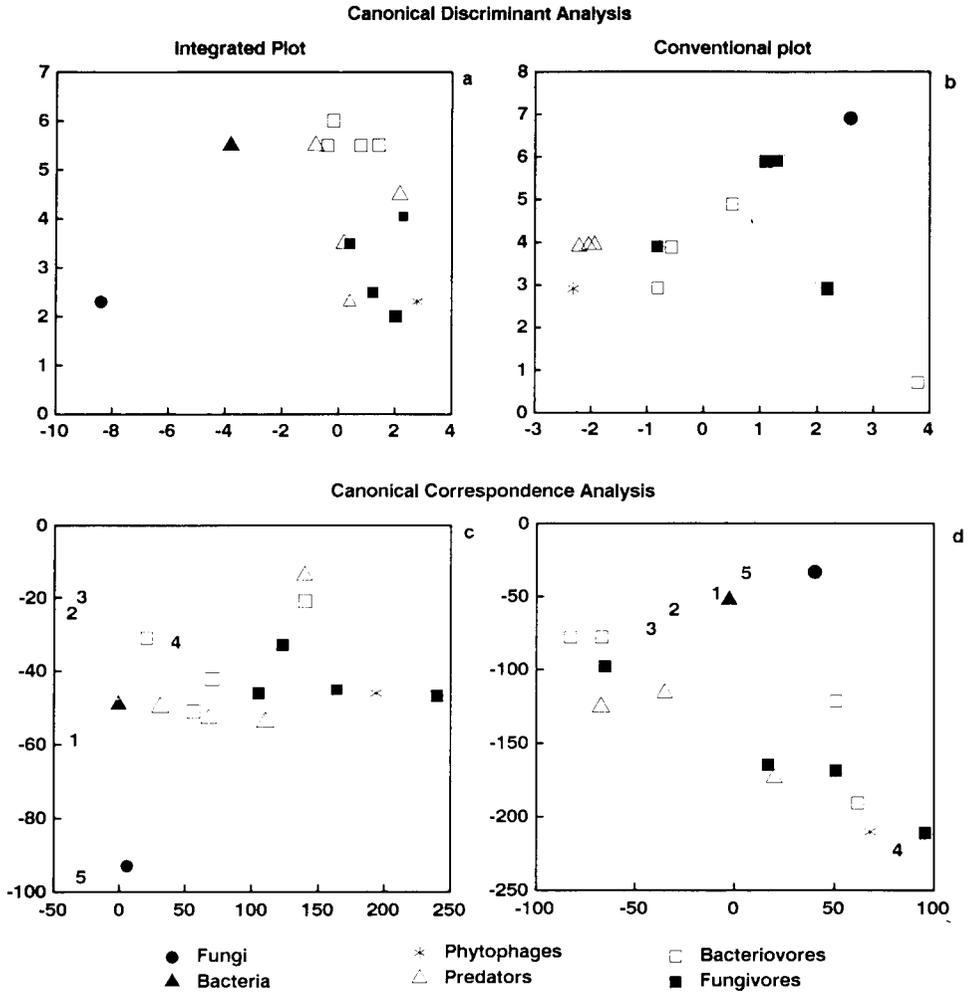


Fig. 4. Scatter plots of the first and second canonical variables of the canonical discriminant analysis (CDA) and the canonical correspondence analysis (CCA) for the categories of functional groups based on food choice and trophic level. (a) CDA, integrated plot; (b) CDA, conventional plot; (c) CCA, integrated plot; (d) CCA, conventional plot. Numbers in the CCA biplots refer to sampling date: 1 = 18 April; 2 = 20 June; 3 = 30 July; 4 = 19 August; 5 = 18 November.

conventional plot, such a pattern could not be identified. The MANOVA indicated that there were differences among the categories of functional groups within the integrated plot ( $P < 0.05$ ) but not within the conventional plot. Therefore, we restricted our use of Hotelling's  $T^2$  to the integrated plot. For the integrated plot, Hotelling's  $T^2$  indicated that the bacteria and fungi exhibited different dynamics, and both groups differed from all consumers (Table 1). The dynamics of the bacterial feeders were different from those of the fungal feeders. Root feeders differed from

Table 1. Matrix indicating which categories of functional groups were different from one another in the canonical discriminant analysis (CDA). Test based on Hotelling's  $T^2$ , where  $T^2 \sim F(1, n_1 + n_2 - 2)$ .

Category of functional groups <sup>1</sup>	1	2	3	4	5	6
1. Bacteria	-					
2. Fungi	**	-				
3. Bacteriovores	**	**	-			
4. Fungivores	**	**	**	-		
5. Phytophages	**	**	*	ns	-	
6. Predators	**	**	ns	ns	ns	-

<sup>1</sup> The number in the row for each category of functional groups corresponds to the number in the column.

\* =  $P < 0.05$ , \*\* =  $P < 0.01$ , ns = not significant.

fungi, bacteria, and bacteriovores, but not from fungivores or predators. Predator dynamics did not differ from the dynamics of consumers of fungi, bacteria or plant roots.

#### Canonical correspondence analysis

The biplots produced by the CCA showed a pattern which bore a resemblance to the patterns generated by the CDA (Fig. 4): in the integrated plot the fungivores were separated from the bacteriovores, indicating different dynamics. To provide a statistical basis for these differences in the integrated plot, Hotelling's  $T^2$  was calculated from the Mahalanobis distances between the groups, with the same drawback as with the CDA: no real replicates were available to calculate the variances within categories of functional groups (Table 2). This test revealed the same pattern of statistically significant differences among the six categories of functional groups, but these differences were less pronounced than in the CDA. This was to be expected, as CDA maximized the differences between pre-designated aggregations of func-

Table 2. Matrix indicating which categories of functional groups in the integrated plot were different from one another in the canonical correspondence analysis. Test based on Hotelling's  $T^2$ , calculated from the first  $p$  axes ( $p = 4$ ), where  $T^2 \sim F(p, \sum n_i - p - 1)$ .

Category of functional groups <sup>1</sup>	1	2	3	4	5	6
1. Bacteria	-					
2. Fungi	*	-				
3. Bacteriovores	x	**	-			
4. Fungivores	*	**	x	-		
5. Phytophages	*	**	x	ns	-	
6. Predators	*	**	ns	ns	x	-

<sup>1</sup>The number in the row for each category of functional groups corresponds to the number in the column.

x =  $P < 0.10$ , \* =  $P < 0.05$ , \*\* =  $P < 0.01$ , ns = not significant.

tional groups, whereas CCA only related the distribution of functional groups to the explanatory variables provided without using prior information about grouping. In the conventional plot, the distance between bacteriovores and fungivores was not significant. The CCA biplots also relate sampling date to the distribution pattern of the groups (Fig. 4), although the interpretation of this relation is not very straightforward. For example, in the biplot of the integrated plot (Fig. 4c) the fungi are near sampling date 5 on which the fungi reached their maximum density, showing a contrast between summer (sampling dates 2, 3, and 4) and autumn (sampling date 5), whereas spring (sampling date 1) was intermediate (see also Fig. 2).

Table 3. Relative importance of the bacteria, fungi, and root energy source (in percentages) of the functional groups in the integrated and conventional plot.

	Integrated plot			Conventional plot		
	bacteria	fungi	root	bacteria	fungi	root
Bacteria	100			100		
Fungi		100			100	
Phytophagous nematodes			100			100
Bacteriophagous nematodes	100			100		
Fungivorous nematodes		100			100	
Predatory nematodes	88	1	11	94	2	4
Oribatida		100			100	
Prostigmata		100			100	
Bacteriophagous mites	100			100		
Nematophagous mites	78	3	19	86	5	9
Predatory mites	45	44	11	33	64	3
Substrate-feeding collembola		100			100	
Predatory collembola	78	3	19	-	-	-
Amoebae	100			100		
Flagellates	100			100		

Table 4. The biomass estimates of bacteria and fungi, and flux rates from the bacterial and fungal energy source; per depth: 0-10 cm and 10-25 cm. Data are standardized per 10 cm depth: biomass (kg N per ha per 10 cm); flux rate (kg N per ha per 10 cm per year).

Depth	Biomass		Flux rate	
	conventional	integrated	conventional	integrated
<i>Bacteria</i>				
0-10 cm	61	93	30	55
10-25 cm	68	76	30	25
<i>Fungi</i>				
0-10 cm	1.14	2.09	0.70	0.85
10-25 cm	1.33	1.71	0.70	0.55

*Analysis of nitrogen flux rates*

The nitrogen flux rates estimated with the simulation model were sorted according to the basic energy sources of the food web: bacteria (detritus), fungi (detritus) and roots (primary production), as a means of summarizing the collective activity of consumers and predators in the food web (Table 3). It appeared that the relative importance of the different energy sources for the polyphagous predators do not reflect the great differences in the biomass-N of the energy sources (the ratio bacteria:fungi:root feeders is approximately 10:1:0.01). Subsequently we calculated the total flux rates derived from the bacterial and fungal energy sources. The ratio of the nitrogen flux rates from the bacteria and fungi was similar to the ratio of the bacterial and the fungal biomass (Table 4). This is not a trivial result, since the calculations of the flux rates depended on the density of the consumers rather than on density of bacteria or fungi. However, the flux rates showed greater spatial heterogeneity than the biomass estimates (Table 4, Fig. 5). In the conventional plot, flux rates

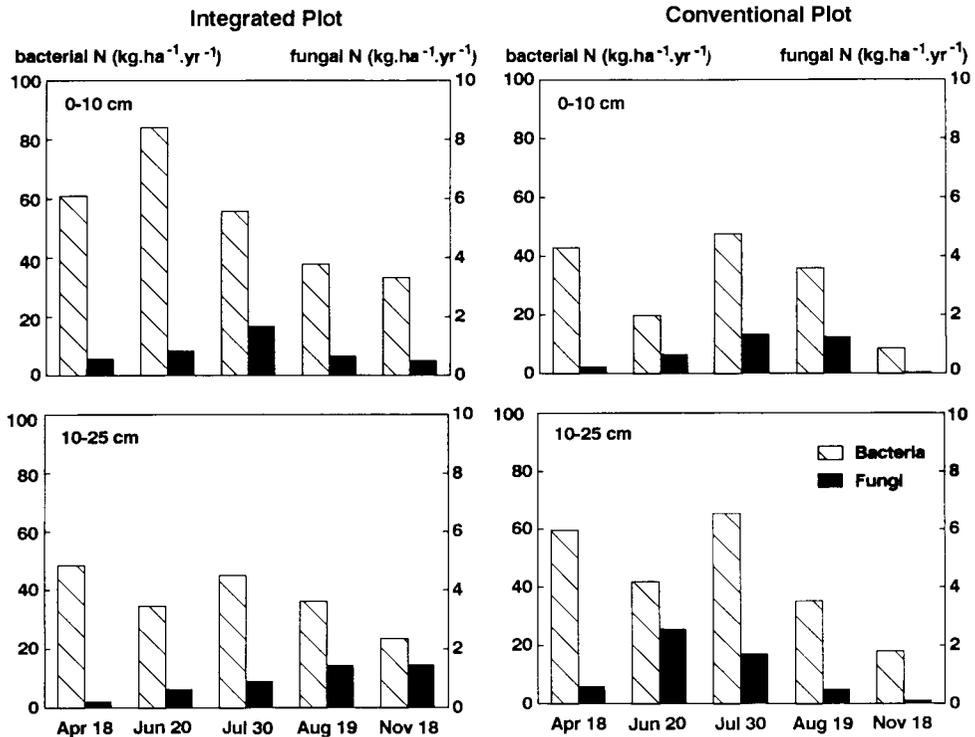


Fig. 5. Bar graphs of the cumulative N flux (kg N ha<sup>-1</sup> yr<sup>-1</sup>) from the bacterial and fungal energy source for the conventional and integrated plot. The upper graphs represent the 0-10 cm depth, while the lower graphs represent the 10-25 cm depth. The estimates in the 10-25 cm depth were not standardized to a 10 cm increment like the estimates in Table 4.

from bacteria and fungi (kg N per ha per 10 cm per year) did not appear to differ between depth, whereas in the integrated plot the flux rates in the top layer (0-10 cm) clearly exceeded the rate in the lower layer (10-25 cm). This result is coinciding with differences in depth of soil tillage: 12 cm cultivator in the integrated plot and 20 cm plough in the conventional plot, and the distribution of organic matter: higher organic matter content in the integrated plot concentrated in the upper layer, and lower levels in the conventional plot homogeneously distributed between the two layers (Brussaard et al., 1988).

## Discussion

The analysis presented in this paper constitutes a case study and conclusions should be formulated with caution, especially for the following reasons. There were no true replications of the food webs, nor of the management practices, and the management practices were confounded with plot history. The functional groups within the categories of functional groups, as used in the CDA and CCA, were considered as replications. All analyses are based on the biomass estimates of the functional groups, and the outcome of the analyses is very sensitive to the accuracy of these data. For some important groups (i.e. bacteria, fungi, protozoa) the methods to estimate biomass carry considerable uncertainties.

The analysis of the Lovinkhoeve food webs presented here suggests that functional groups with similar food sources may exhibit similar dynamics. In the integrated plot, with the strongest evidence of temporal clustering of functional groups, this clustering appeared to be based more on food source rather than on taxonomy. For example, the bacteriophagous mites had dynamics in common with amoebae, flagellates, and bacteria rather than with other groups of mites. Bacteriophagous nematodes showed closer affinity to other bacteriovores, while fungivorous nematodes clustered with fungivorous mites and collembola. The predators (functional groups that occupy trophic positions IV and V) appear to span the range of dynamics of their prey (Figs 3 and 4). The separation of the consumers of bacteria and fungi in time observed in the integrated plot may be due to several factors. Bacteria and fungi differ in their rates of growth and their responses to environmental variables, e.g. moisture, temperature, and disturbances within soil (Moore & Hunt, 1988; Allen-Morley & Coleman, 1989). Consumers of bacteria and fungi may simply be responding to changes in the abundance of their food source.

The estimates of nitrogen flux rates supported the indication that the decomposer subsystems within the integrated and conventional plot are dominated by the bacterial energy source. This dominance of bacteria may be reflecting the history of the Lovinkhoeve soils. Bacteria and their consumers may have simply established in the site more readily than the fungi and their consumers (M. Christensen, pers. comm.). The levels of bacterial and fungal biomass-N and the flux rates of nitrogen originating from fungi and bacteria were higher in the integrated plot than in the conventional plot. The higher biomass and flux rates in the integrated plot over the conventional plot are probably due to differences in the organic matter content of the soils (Brussaard et al., 1988; Kooistra et al., 1989).

The analysis of the nitrogen flux rates by depth indicated that in the conventional plot there was no difference between the top 10 cm and the 10-25 cm layer for the flux rates originating from the bacterial and the fungal energy source (Table 4, Fig. 5), whereas in the integrated plot proportionally more material flow occurred in the upper 10 cm than in the 10-25 cm layer. The differences in the depth distributions of the flux rates between the management practices and within the integrated plot is probably related to the depth of tillage for each practice: 20 cm in the conventional plot and 12 cm in the integrated plot.

For agricultural systems, Elliott & Coleman (1988) suggested that more efficient use of agroecosystems may be achieved via reduced tillage to maintain optimal soil structure, reduced inputs of biocides, and less intensive management in order to better manage microbial populations. An objective of the research efforts by Elliott & Coleman (1988) and Brussaard et al. (1988) is to manage microbial populations in order to attune nitrogen dynamics to plant growth. To this end, in addition to understanding microbial dynamics, the dynamics of the micro- and mesofauna should also be studied in view of their significant contribution to mineralization (Clarholm, 1985; Ingham et al., 1985; Hunt et al., 1987; Moore et al., 1988). These efforts are by necessity whole-systems approaches, and the techniques outlined here may assist in untangling the network of feeding interactions that constitute the mineralization process.

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## **A simple model of P uptake by crops as a possible basis for P fertilizer recommendations**

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### **Abstract**

In the Netherlands the  $P_w$  value, based on an extraction of soil P with water, is used as a basis for P-fertilizer recommendations for arable crops. Using a simple, mechanistic model of P transport in the soil the  $P_w$  value required for adequate P uptake by crops can be calculated on the basis of daily uptake requirements, root area index, P-adsorption isotherms and total amount of P taken up during a growing season. Calculated  $P_w$  values for adequate uptake are in the same range as the present recommendation scheme based on field experiments. Possible refinements of the model are discussed. For each soil the  $P_w$  value can be calculated that corresponds to the P concentrations in the soil solution according to standards set to reduce environmental pollution. Our model predicts that, unless the root area index of non-cereal crops is considerably improved, these standards cannot be met in the plough layer without affecting crop production levels. Calculations show that the present method of determining the  $P_w$  value yields a reasonable compromise between a measurement of intensity and capacity of P supply in the soil.

*Keywords:* root length density, root area index, phosphorus availability, phosphate adsorption, barley, bean, maize, onion, potato, sugar beet, wheat

### **Introduction**

The major aim in soil fertility research in the Netherlands in the past century has been to raise existing soil fertility levels to the point where nutrient supply is non-limiting. Increasing the phosphorus supply was one of the first priorities in N.W. Europe, and still is in many tropical countries. The first question, still relevant, was at what soil fertility level supply is non-limiting. In our present definition this is the level where, per unit root, the supply is equal to demand throughout the growing season. The critical level thus depends on plant factors that affect total demand, on the size of the root system, and on soil factors determining supply.

For a fertilizer recommendation scheme we also need to know how serious growth reductions are at soil fertility levels slightly below the critical level and what the relative effectiveness of various soil amendments (e.g. manure, cattle slurry) is. Furthermore, current fertilizer recommendation schemes are based on fertilizer/product

price ratios, on maintenance of desirable soil fertility levels and on the crop rotation used. Nowadays, avoidance of environmental pollution should be included in the recommendations. In the present Dutch national environmental policy, a P concentration not exceeding  $0.15 \text{ mg l}^{-1}$  in surface water and  $0.40 \text{ mg l}^{-1}$  in the upper m of the groundwater on sandy soils (van Duijvenbooden et al., 1989) is aimed at. The first question we will deal with is whether or not these environmental standards are reconcilable with adequate P supply to crops.

In view of the large number of factors influencing both supply and demand, it seems unlikely that any single soil test can be used for establishing a criterion for adequacy of P supply to crops. Still, establishment of simple soil test procedures from which the amount of 'available' nutrients can be determined for each crop, preferably without further information on soil factors, has been the focus of much research and debate. In the history of Dutch P fertility research a number of extraction techniques have been used, leading to a water extraction method known as the Pw value technique (van der Paauw, 1971). It gives the amount of phosphate extractable from  $1 \text{ cm}^3$  of soil with 60 ml of water after 22 h of incubation with 2 ml water (Sissingh, 1971). It is expressed in  $\text{mg P}_2\text{O}_5$  per liter soil and is currently used for arable soils. In the current scheme (van der Paauw, 1973) a target Pw value of 30 is used for diluvial sandy soils, cut-over peat soils, basin clay and loess, and of 25 for marine clays and alluvial sands, for crop rotations with potato as the crop requiring the highest P status of the soil. When the Pw value is equal to or slightly above this target value the recommended rates of P fertilization for a crop rotation slightly exceed the amount of P expected to be removed with the products harvested. If the Pw value is higher than the target value, the recommended rate of P fertilization is lower and the Pw value will consequently decrease; if the Pw value is below the target, the recommended rate of P fertilization considerably exceeds expected removal. In the recommendation scheme, four groups of crops are identified based both on differences in P-response curves and differences in fertilizer/crop price ratios. From the scheme a Pw value can be derived for each crop where expected crop removal and recommended fertilization are equal. This Pw value we will indicate as the apparent equilibrium point of the recommendation scheme. The second question we will discuss is to what extent the P status of the soil obtained at the apparent equilibrium point of the recommendation scheme for each crop, is in agreement with results of a simple, mechanistic model (de Willigen & van Noordwijk, 1987) of P transport in soil and uptake by roots. The third question we will deal with is whether it is possible to obtain acceptable results with a single soil test, in spite of the large differences between soils in buffer capacity for P. Finally, we will discuss which process description is minimally required to predict the long-term P balance of arable soils.

## **Models and parameters**

### *Calculation of the Pw value from adsorption isotherms*

Inorganic phosphorus in the soil can be considered to consist of three fractions:

phosphorus in the soil solution, phosphorus in the labile pool and non-labile phosphorus. The labile phosphorus mainly consists — we shall assume exclusively — of reversibly adsorbed phosphate (Olsen & Khasawneh, 1980). The non-labile phosphorus is contained in poorly soluble minerals and/or is irreversibly adsorbed. Transfer from the non-labile to the labile pool and vice versa occurs so slowly that it may be neglected during a growing season, as a first approximation (Barber, 1984). The relation between labile phosphate and phosphates in solution can be given by an adsorption isotherm. For our present purpose, adsorption can be considered as instantaneous (de Willigen, 1981).

Figure 1 gives phosphate adsorption isotherms for eight Dutch soils, determined in 0.005 M CaCl<sub>2</sub> for 24 h, at a solution-to-soil volume ratio of 20. These isotherms can be described by a two-site Langmuir equation, for which no mechanistic interpretation is given here (Holford & Mattingley, 1975):

$$C_a = \frac{A_1 B_1 C}{1 + B_1 C} + \frac{A_2 B_2 C}{1 + B_2 C} \tag{1}$$

where:

- $C_a$  = adsorbed phosphate in g P dm<sup>-3</sup> soil
- $C$  = the concentration of phosphate in the soil solution in g P l<sup>-1</sup>
- $A_1, A_2$  = adsorption maxima in g dm<sup>-3</sup>
- $B_1, B_2$  = parameters in l g<sup>-1</sup>

The parameters fitted to the adsorption isotherms in Figure 1 are listed in Table 1. The slope of the adsorption isotherm ( $dC_a/dC$ ) can be defined as buffer capacity. It has a maximum for  $C = 0$ , equal to  $K_a = A_1 B_1 + A_2 B_2$ .  $K_a$  varies 28-fold in

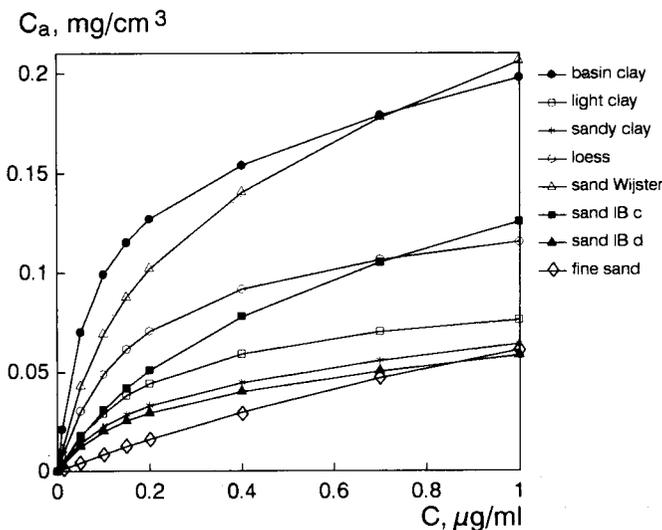


Fig. 1. Adsorption isotherms for eight Dutch soils; for parameters see Table 1.

Table 1. Parameters of 24-hour P-adsorption isotherms for eleven Dutch soils, arranged according to maximum buffer capacity  $K_a$ ; Pw(n1) and Pw(n2) are the calculated Pw values (in  $P_2O_5$ , mg l<sup>-1</sup>) corresponding to the standard of a solution P concentration of 0.15 and 0.4 mg l<sup>-1</sup>, respectively; the ratio  $r_e$ , of the bulk density during the determination of the Pw value and the bulk density in the field, the assumed water content  $\theta$  at field capacity is shown as well as the resulting effective diffusion constant,  $D_e$ , used in the calculations for Table 3.

Soil type <sup>1</sup>	$B_1$ (l g <sup>-1</sup> )	$B_2$ (l g <sup>-1</sup> )	$A_1$ (g dm <sup>-3</sup> )	$A_2$ (g dm <sup>-3</sup> )	$K_a$ (l dm <sup>-3</sup> )	Pw standards		$r_e$	$\theta$ (dm <sup>3</sup> dm <sup>-3</sup> )	$D_e$ (cm <sup>2</sup> d <sup>-1</sup> )
						n1	n2			
Fine sand	500	8.5	0.16	0.91	88	12	29	1	0.25	0.084
Sand IB d	8056	142	0.039	0.19	342	14	29	0.77	0.25	0.084
Sand IB c	4430	340	0.073	0.26	413	17	40	0.74	0.25	0.084
Loess	6600	44	0.12	0.26	439	16	34	1	0.40	0.14
Sand Wijster	7860	220	0.133	0.49	1150	17	40	1	0.25	0.084
Sandy clay	8590	177	0.043	0.17	1250	15	30	0.77	0.40	0.14
Light clay	5000	20	0.087	0.18	1570	15	30	1	0.40	0.14
Basin clay	16000	130	0.15	0.49	2460	17	37	1	0.40	0.14

<sup>1</sup> Origin of the soils used: *fine sand*: Zeijen; *sand IB c and d*: IB-farm Haren, adjacent fields; *loess*: Wijnandsrade; *sand Wijster*: IB 1920; *sandy clay*: Noordoostpolder, Lovinkhoeve IB 0013; *light clay*: Warffum; *basin clay*: Hedel.

the soils examined. The maximum adsorption  $A_1 + A_2$  occurs as  $c \rightarrow \infty$  and varies 5-fold, from 0.21 for the sandy clay to 1.07 g dm<sup>-3</sup> for the fine sand.

As described by de Willigen & van Noordwijk (1978), the amount of P extracted during measurement of the Pw value can be calculated from the adsorption isotherm of a soil and the total amount of labile P measured with exchange resin or with non-limiting amounts of iron-hydroxide-impregnated filter paper (van der Zee et al., 1987; Menon et al., 1989) from a well-mixed slurry (water-to-soil volume ratio 20, in 0.005 M CaCl<sub>2</sub>) in 24 h. The calculation is based on the assumption that the amount of labile P does not change during extraction, that desorption isotherms are equal to adsorption isotherms and that effects of background electrolyte concentration on the adsorption/desorption process may be neglected. These assumptions lead to:

$$S = C_a + \theta C = C_a^* + V_w C^* \quad (2)$$

where:

$S$  = total amount of labile phosphorus per dm<sup>3</sup> of soil (g dm<sup>-3</sup>)

$\theta$  = water content of the soil (dm<sup>3</sup> dm<sup>-3</sup>)

$V_w$  = volume ratio of water to soil used during extraction;  $V_w = 60$  for the Pw value as defined by Sissingh (1971)

$C_a^*$ ,  $C^*$  = equivalent of  $C_a$  and  $C$ , during determination of the Pw value

Combination of Equations 1 and 2 gives a cubic equation in  $C^*$ , which can be solved iteratively, given the parameters of the adsorption isotherm and  $S$ . The Pw value, expressed in mg P<sub>2</sub>O<sub>5</sub> per liter of soil, is calculated as  $1000 \times (142/62) \times C^* \times V_w$ .

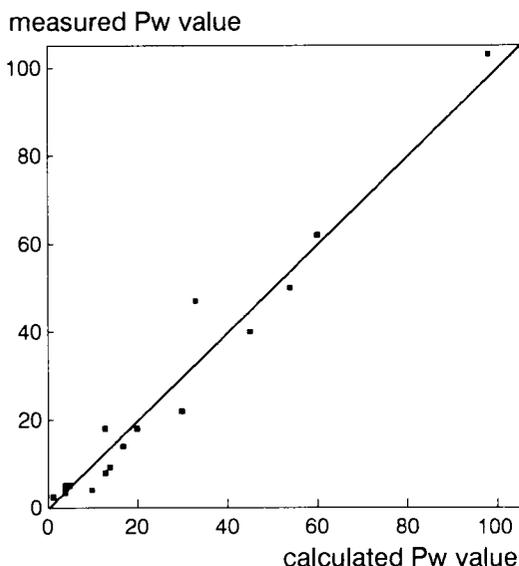


Fig. 2. Calculated versus measured Pw values; for several soils more than one P level is included; data on three soils not mentioned in Table 1 are included.

With increasing  $V_w$ , more P would be extracted from the soil, but the degree to which this happens would depend on soil type and P status of the soil.

Figure 2 shows that calculated Pw values agree well with measured Pw values for the same soils. We will therefore assume that Pw values can be calculated on the basis of adsorption isotherms and total amount of labile P. In the calculations for Figure 2 we used the bulk density of each soil as measured during a Pw value determination; for further calculations we used the bulk density under field conditions, insofar as estimates were available.

#### *Calculations of P uptake by crops*

The total amount of labile P is available for instantaneous uptake by a root system of infinite density and negligible volume. Root systems of finite density can only extract a certain fraction from the soil at the rate required for crop growth (the unrestrictedly available amount). The remainder is restrictedly available, i.e. at a rate determined by transport processes in the soil (de Willigen & van Noordwijk, 1987). To predict what available amount in the soil is necessary to have just sufficient unrestrictedly available P in the soil, we have to specify crop demand, root density and activity.

Figure 3 shows the time course of P uptake by potatoes with adequate or suboptimal P supply, as measured by van der Paauw (1948). By far the largest part of the dry matter produced by a crop is synthesized during the linear growth period. The major part of P is also taken up at a constant daily rate. The same is true for other

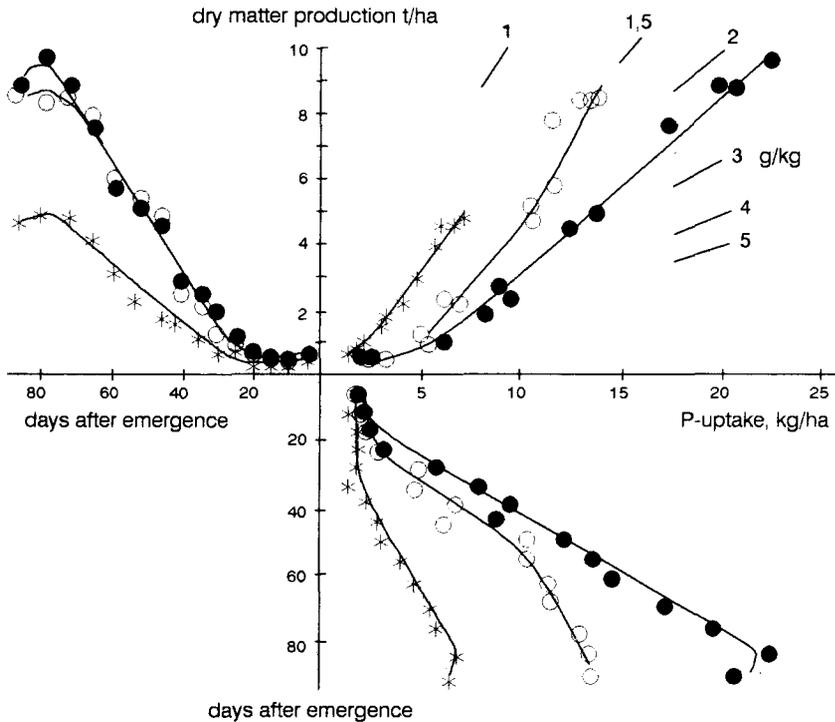


Fig. 3. Time course of P uptake and dry matter production of potato at three levels of P supply in the soil (data from van der Pauw, 1948). In quadrant I, P concentrations of 1 to 5 ‰ are indicated as slopes.

crops and other nutrients as follows from Figure 4, based on measurements by van Itallie (1937) of crops under non-limiting nutrition. Uptake is generally two weeks ahead of dry matter production, so P contents are gradually decreasing despite constant daily dry matter production and P uptake. As the root system is at first approximation constant in size during the linear growth period of the crop, the daily uptake requirement per unit root length is constant for a considerable length of time (de Willigen & van Noordwijk, 1987).

Actual uptake patterns such as in Figure 3 cannot be explained by mechanistic models of nutrient uptake where the uptake rate is described as a function of external concentration (Nye & Tinker, 1977; Barber, 1984), unless the physiological parameters governing uptake are described as a function of internal P content in the plant or are derived as a function of plant age for plants growing under identical field conditions. Internal regulation of P uptake by the plant (Alberda, 1948) has recently been rediscovered by plant physiologists (Clarkson, 1985). In our model (van Noordwijk & de Willigen, 1979; de Willigen & van Noordwijk, 1987) we assume internal regulation of uptake rates to be complete and we describe the uptake rate as either demand-governed (equal to total demand divided by total root length) or supply-governed (equal to supply by mass flow and diffusion to a cylindrical 0-

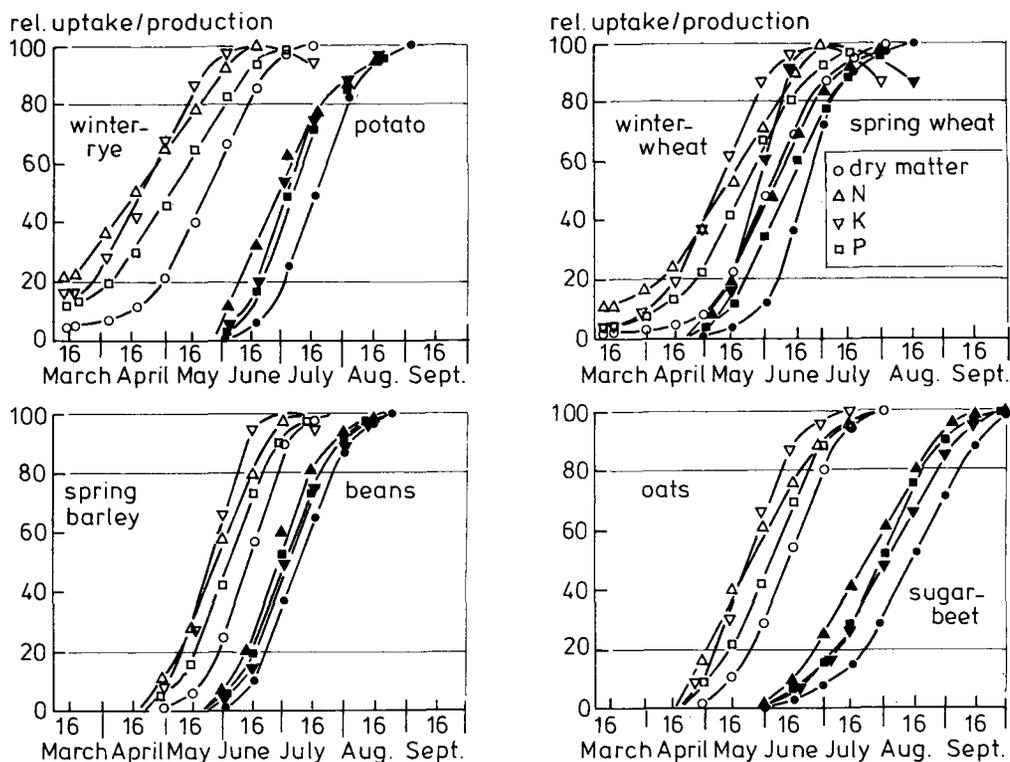


Fig. 4. Time course of N, P and K uptake and dry matter production of eight crops under non-restricted supply (van Itallie, 1937).

sink). We further assume roots to be regularly distributed and in complete contact with the soil.

Phosphorus uptake from a soil is highly dependent on root development of the crop. In two stages of crop development, P uptake may lag behind P demand for maximum growth rates: during initial growth, when the demand per unit root length usually is high, and during the second half of the growing season, when root growth stops and the root environment has been partially depleted, while P demand continues. We will concentrate here on the P level of the soil required to avoid deficiency in the second half of the growing season, but for crops with high shoot:root ratios in the initial stages (especially high shoot weight per unit root length) the P level initially required may be higher than that calculated here.

As shown elsewhere (de Willigen & van Noordwijk, 1987), the assumption of a constant daily uptake requirement per unit root surface area leads to the development of steady rate profiles of the concentration around each root, for nutrients where the fraction adsorbed is independent of the concentration. For phosphate with a non-linear adsorption isotherm we found that the concentration in the soil

solution around each root can be satisfactorily approximated by a steady-rate profile as well. At the time when the concentration at the root surface decreased to  $C_{\min}$ , the steady-rate profile is given by:

$$C(r) = C_{\min} r^{2\nu} + \frac{F_a R_o}{D} \left[ \frac{\varrho^{2\nu+2} (r^{2\nu} - 1)}{2\nu (\varrho^{2\nu+2} - 1)} + \frac{r^{2\nu} - r^{2\nu+2}}{2 (\varrho^{2\nu+2} - 1)} \right] \quad (3)$$

where:

$C(r)$  = concentration at distance  $r$  (mg l<sup>-1</sup>)

$C_{\min}$  = concentration required at the root surface to maintain sufficiently high uptake rates (mg l<sup>-1</sup>)

$r$  =  $R/R_o$  = dimensionless distance in the soil cylinder

$R_o$  = root radius (cm)

$\varrho$  =  $(R_o \sqrt{\pi L_{rv}})^{-1}$

$L_{rv}$  = root length density (cm cm<sup>-3</sup>)

$F_a$  = required uptake rate per unit root surface area ( $\mu\text{g cm}^{-2} \text{ day}^{-1}$ )

$D$  = effective diffusion constant (cm<sup>2</sup> day<sup>-1</sup>)

$\nu$  =  $-E_a R_o / 2D$

$E_a$  = transpiration rate per unit root surface area (cm day<sup>-1</sup>)

The amount  $S$  of available P which should be present in the soil at the start of the growing season to allow uptake at the required rate during the whole growing season can now be formulated as:

$$S = U + T + M \quad (4)$$

where  $U$  is total crop uptake during the growing season,  $T$  is the amount required to allow a sufficiently high rate of P transport to the root surface and  $M$  is the

Table 2. Estimates of parameters determining the uptake required per unit root surface area for seven crops. Total P uptake by each crop is based on Anon. (1989). The period in which 60 % of total uptake occurs,  $t_{20-80}$ , was derived from Fig. 3. Root length data,  $L_{rv}$ , based on de Willigen & van Noordwijk (1987), and estimates of root radius,  $R_o$  partly based on Jungk & Claassen (1989), were used to calculate the root area index, RAI. Daily demand during the linear growth phase,  $A$ , has been combined with root data to obtain the required inflow per unit root length,  $I_1$ , and the required flux per unit root surface area,  $F_a$ .

	P removal (kg ha <sup>-1</sup> )	P uptake (kg ha <sup>-1</sup> )	$t_{20-80}$ (d)	$A$ (kg ha <sup>-1</sup> )	$L_{rv}$ (cm cm <sup>-3</sup> )	$R_o$ (mm)	RAI	$I_1$ ( $\mu\text{g cm}^{-1}$ d <sup>-1</sup> )	$F_a$ ( $\mu\text{g cm}^{-2}$ d <sup>-1</sup> )
Bean	18	20	34	0.35	0.8	0.15	1.9	0.175	1.86
Potato	24	34	31	0.65	1.5	0.15	3.5	0.173	1.84
Onion	20	23	45	0.31	0.8	0.25	2.5	0.155	0.99
Sugar beet	41	42	43	0.58	2	0.10	3.1	0.116	1.23
Maize	35	37	45	0.50	2.5	0.10	3.9	0.080	0.85
Barley	19	23	33	0.41	4	0.10	6.3	0.041	0.65
Wheat	24	28	52	0.32	6	0.10	9.4	0.022	0.35

amount corresponding to the term with  $C_{\min}$ . For phosphate,  $C_{\min}$  is approximately  $1 \mu\text{mol l}^{-1}$  or  $0.031 \text{ mg l}^{-1}$  (de Willigen & van Noordwijk, 1987). The amount  $T + M$  can be calculated by substitution of Equation 3 into Equations 1 and 2, and integration of the resulting equation over the soil cylinder. The amount  $T + M$  (in  $\text{g dm}^{-3}$ ) is given by the integral:

$$T + M = \frac{1}{1000 (\rho^2 - 1)} \int_1^{\rho} 2r(C_a + \Theta C) dr \quad (5)$$

where  $C$  is given by Equation 3 and  $C_a$  by Equation 1. The integral can be evaluated by numerical integration.

By assuming average values for the respective parameters for seven crops (Table 2), we can now calculate the required amounts of available P and the corresponding Pw values on the various soil types. Daily uptake requirement in the period of constant daily uptake was estimated from the number of days  $t_{20-80}$  between 20 and 80 % of the cumulative uptake in Figure 4 and realistic values of total uptake. We assumed for each crop a P-containing plough layer of 25 cm with homogeneously distributed roots, with complete root-soil contact but no root hairs penetrating the soil. An average root diameter was estimated for each crop. The water content of the soil has a major effect on transport by diffusion; we took the estimated value at field capacity (pF 2.0) for each soil. Calculated Pw values corresponding to  $S$  as defined above are listed in Table 3 for each crop/soil combination. For comparison

Table 3. Calculated values of the Pw value required in eight soils at field capacity for non-P-limited growth of seven crops. For comparison the range of Pw values is included which are obtained after P fertilization when the soil is at the 'apparent equilibrium' point where recommended P application equals the expected uptake by the crop in the current P-recommendation scheme (Anon., 1986). The scheme distinguishes two classes of soils: diluvial sands, cut-over peat soils, loess and basin clay (I) and marine clay soils and alluvial sands (II).

	Bean	Potato	Onion	Sugarbeet	Maize	Barley	Wheat
I. Wijster sand	88	87	72	73	53	29	19
IB sand c	68	54	45	46	34	19	13
Fine sand	71	73	59	64	48	27	21
IB sand d	41	44	35	39	31	18	14
Basin clay	58	59	48	51	38	21	14
Loess	51	54	44	49	38	21	15
II. Light clay	46	50	42	48	37	21	16
Sandy clay	32	34	27	31	24	14	11
<i>Current scheme</i>							
Apparent eq. I	63	47	59	33	44	45	24
+ P-fert.	65-72	53-58	64-69	42-51	55-60	50-54	28-34
Apparent eq. II	62	46	59	29	44	31	18
+ P-fert.	70-72	57	69-70	45	60	38	25

the apparent equilibrium points of the present recommendation scheme are given as well as the range of  $P_w$  values resulting for different soils from an addition of P equal to the amount removed in harvested products. Of the three terms in Equation 4, the term  $T$  has the largest value in all situations considered.

## Results

### *P<sub>w</sub> values corresponding to pollution standards*

As shown in Table 1, a P concentration of 0.15 mg l<sup>-1</sup> occurs at different  $P_w$  values in different soils, varying from 18 on the Wijster sand to 12 on the fine sand; the  $P_w$  values corresponding to a concentration of 0.4 mg l<sup>-1</sup> vary between 26 for the IB sand d and 41 for the Wijster sand. Although predictions of P leaching behaviour in soils are more complicated as relatively slow fixation processes have to be taken into account (Raats et al., 1982), the leachate from a sandy soil with a  $P_w$  value higher than the calculated value will have a P concentration exceeding the maximum permissible value. The target values of the present P recommendation scheme for arable crops imply that the inorganic P concentration of the leachate from the plough layer will be higher than allowed in surface water, and for sandy soils slightly higher than allowed in the upper meter of groundwater. As a certain amount of organic P will be present in solution as well, the maximum permissible total P concentration is likely to be exceeded in leachates from a plough layer on sandy soils with a  $P_w$  value above 20. At the (much) higher  $P_w$  values recommended for vegetable crops, environmental standards cannot be met.

### *P<sub>w</sub> values required for different crops*

Table 3 shows that the calculated  $P_w$  values required are of the same order of magnitude as the  $P_w$  values obtained at the apparent equilibrium points of the present P-recommendation schemes. In Figure 5 the average calculated  $P_w$  value for each crop is compared with the average  $P_w$  value according to the recommendation scheme, for the two classes of soils distinguished in the scheme. The calculated values for the different crops allow a distinction between crops with a high and with a low demand similar to that in the present scheme. Table 2 shows that differences among crops in uptake required per unit root surface area are largely determined by differences in root length density. To obtain non-P-limited growth on sandy soils which meet the environmental standards, a potato crop should have a root length density comparable to that of a wheat crop, a nice target for plant breeders.

Empirical evidence shows that barley requires a higher soil P status than wheat. Our calculations confirm the difference as the required influx is higher for barley than for wheat (Jungk & Claassen, 1989) due to a lower root length density of barley (Weaver, 1926; Schjørring & Nielsen, 1987), but the difference we calculated is smaller than the difference in the present recommendation scheme.

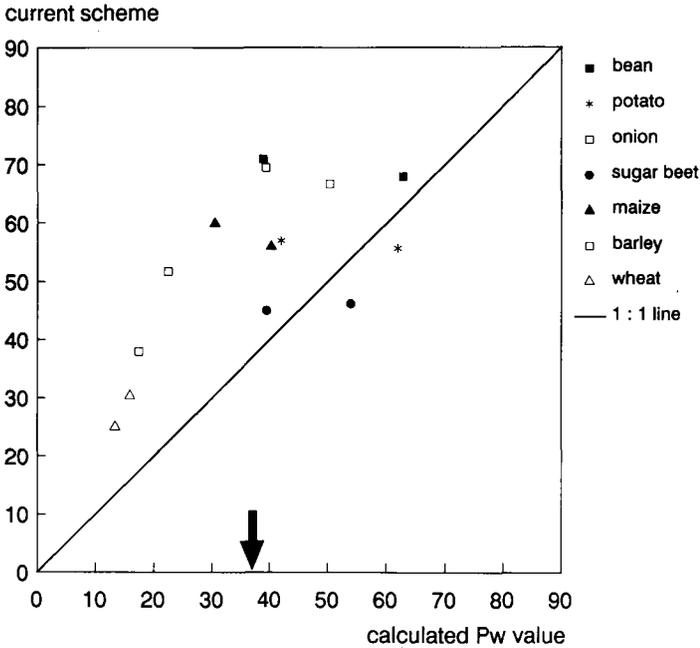


Fig. 5. Comparison of the required Pw value calculated with our simple model and the Pw value resulting from recommended P application at the apparent equilibrium point of the P-recommendation scheme; values are averages for the two classes of soils in the recommendation scheme; the arrow indicates a Pw value for sandy soils where the concentration in the soil solution is in agreement with environmental standards for the upper meter of groundwater.

#### *Pw value as an index of P availability*

The required Pw values calculated with the same crop parameters for different soils show variation. The ratios of highest and lowest value range from 1.9 for wheat to 2.8 for beans. Although this ratio is much smaller than the ratios of highest and lowest  $K_a$  or sorption maximum among the soils, it suggests that, at least for certain crops, fertilizer recommendations cannot be based on a single parameter, such as the Pw value, but should also consider other information, related to the P-adsorption isotherm. A classification by soil types may help to a certain extent, but the two calculations for Haren sand, based on adsorption isotherms for soils collected from adjacent fields, gave a 1.7-fold difference in Pw value required for beans. The performance of the Pw value technique as a compromise between a measurement of *intensity* of P supply (concentration in the soil solution,  $C$ ) and its *capacity* (total amount of labile P,  $C_a$ ) can be judged from our calculations. Required P levels vary more when expressed as capacity than when expressed as intensity. For a number of crops they vary less when expressed as a Pw value than when expressed as a concentration in the soil solution. Based on Equation 2 we calculated the  $Pw(V_w)$  values for different water-to-soil volume ratios  $V_w$  during the extraction,

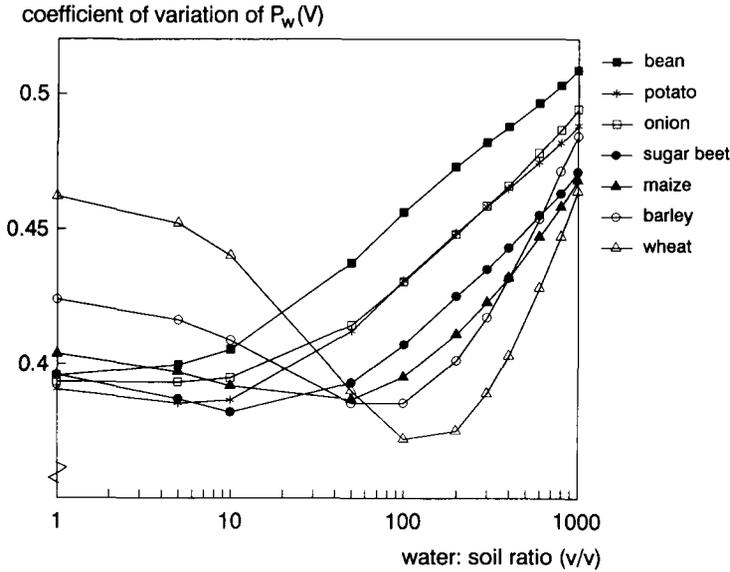


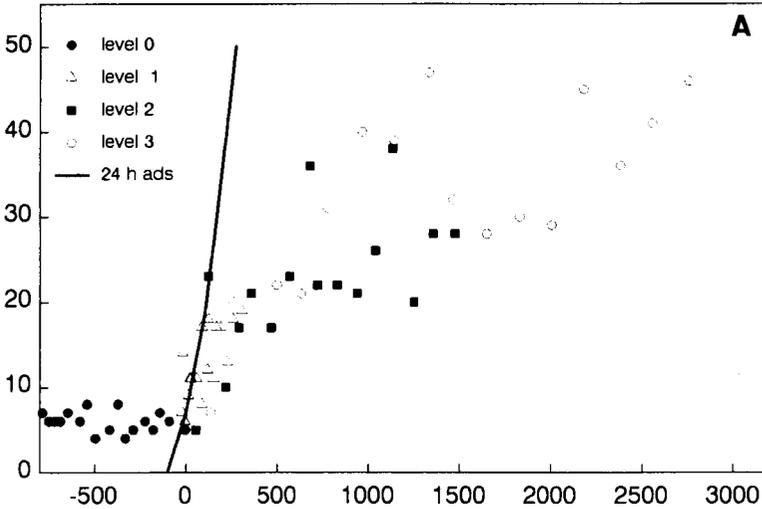
Fig. 6. Coefficient of variation (standard deviation divided by mean) of calculated P status on the various soils (Table 1), when the P status is expressed as  $P_w(V)$  value for different water-to-soil ratios  $V_w$  during the extraction.

at the soil P status calculated to be required for each crop. For infinitely high  $V_w$  a  $P_w(V_w)$  value constitutes a measurement of capacity, for  $V_w$  of about 0.3 it is a measurement of intensity. Figure 6 shows the coefficient of variation of calculated  $P_w(V_w)$  values as a function of  $V_w$ , with a minimum indicating an optimum value of  $V_w$  for each crop. The higher the required uptake per unit root length, the more important intensity becomes and the lower  $V_w$  should be to obtain an optimum basis for a P-recommendation scheme independent of soil type.

#### *Long-term P balance of arable soils*

Figure 7 shows  $P_w$  values measured during a period of 16 years in two long-term P fertilization trials, at various rates of annual P application. Each year the P balance was estimated as the difference (positive or negative) of P added as water-soluble phosphate and P removed in harvested products. In the two graphs, solid lines designate calculated changes in  $P_w$  value if only fertilization and crop uptake would influence the amount of labile P in the soil. The long-term behaviour of the soil differs in two important respects from these calculations: at high P application rates the increase in  $P_w$  value is much smaller, and without P application the decrease in  $P_w$  value is much smaller. In fact, the  $P_w$  value tends to an equilibrium value of about 7 for the sandy loam and about 10 for the Wijster sand. Raats et al. (1982) described P transport in the soil assuming an irreversible fixation process to remove P from the labile pool. Maximum fixation capacity was assumed to be

Pw value sandy clay, IB 0013



Wijster, IB 1920

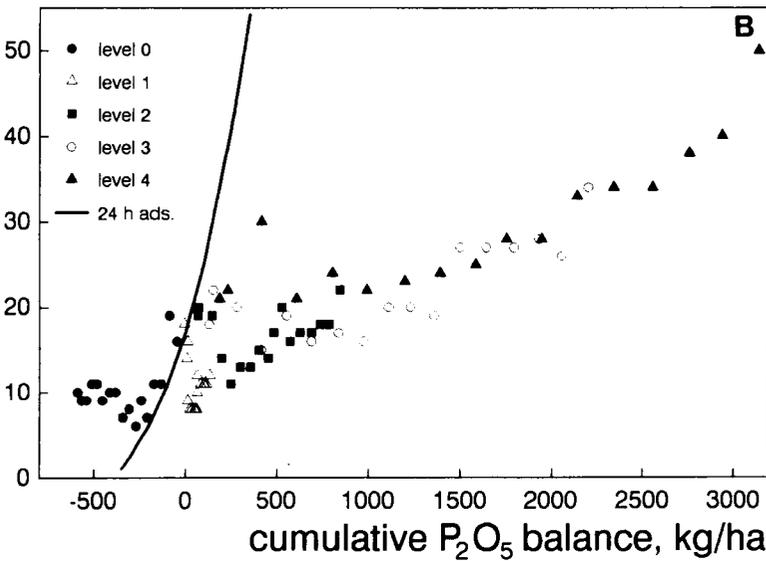


Fig. 7. Pw measurements during a period of 16 years as a function of the P balance of two experimental fields (inputs as water soluble P minus outputs in harvested products). (A) a sandy clay soil in the Noord-oostpolder (Lovinkhoeve, IB 0013); (B) sandy soil in Wijster (IB 1920) at five levels of superphosphate; at four levels of TSP (triple superphosphate). The solid lines were calculated on the basis of 24 h adsorption isotherms.

related to the aluminium and iron content of the soil; the half-life period of fixation was found to be about 30 days for a particular soil (Raats et al., 1982). Such a description may account for the fact that the Pw value increases much more slowly than expected on the basis of 24-h adsorption isotherms; however, it cannot account for the stabilization of the Pw value when no P is applied. For predictions concerning the long-term P balance, which are required for P recommendation scheme and predictions of leaching, both mobilization and immobilization have to be described as reversible processes.

Immobilization implies that a higher initial Pw value is required to reach a sufficiently high Pw value at the end of the growing season, if the value required exceeds the equilibrium Pw value of the soil. Mobilization means that in the root environment, where the root creates a low concentration in the soil solution, additional P appears in the labile pool. For the rate at which this occurs no independent measurements are available as yet. Tentative calculations show that incorporating a mobilization/immobilization process with a time constant of a month or more has little effect on results for a single growing season.

## Discussion

### *Model improvement*

Although our simple model gives results of at least the right order of magnitude, a number of discrepancies exist between calculations and empirical results. These may indicate that the simple model needs refinements, e.g. inclusion of the role of root hairs, mycorrhiza, phosphatase activity in the rhizosphere or pH changes induced by the root. The empirical basis for the P recommendations for crops other than potato is rather weak, however, and the between-years variation in P response on each site is considerable. Hence, refutation of the simple model and incorporation of refinements should be based on individual field experiments where the parameters necessary for a rigorous test are known.

Our calculated P requirements for soils at field capacity are slightly below empirical values; under drier conditions our model would calculate higher values because of lower effective diffusion constants. Parameter values such as root length densities where chosen in the range documented in the literature; in specific experiments, both higher and lower root length densities are possible; present data are inadequate to establish reliable ranges of values for each crop under field conditions. The role of root hairs was neglected in our calculation, but we assumed complete soil-root contact, which is realistic only if roots form sufficient root hairs when they grow in a gap or channel larger than their own diameter. The role of mycorrhizal hyphae as an extension of roots was neglected so far: the P levels required by mycorrhizal crops may be considerably lower. P uptake from the soil below the plough layer was neglected; it will be usually low as soil P levels as well as root length density in deeper layers will be considerably lower than those in the plough layer, but exceptions exist. Root turnover, simultaneous new root growth and root death in the same soil layer, will have no effect on the possible P uptake in our model, as it does not affect

the average value of  $F_a$  which governs the shape of the steady-rate concentration profile. Still, when root turnover is rapid, our steady-rate approximation will not be valid and more P can be taken up. Available evidence so far shows that root turnover can be considerable for sugar beet (approximately 50 % per season) but not for wheat (12 %) (de Willigen & van Noordwijk, 1987). Microbiological interactions in the rhizosphere influencing P availability from fertilizers have been known for a long time (Gerritse, 1948; Kucey et al., 1989). Recently, buckwheat, clover and cereals were reported to excrete phosphatases which can digest organic P (Amann & Amberger, 1989; Tarafdar & Claassen, 1988). In soils rich in organic P (Gerritse et al., 1982) this may be relevant and allow the plants to use P not included in our calculations and not measured in the  $P_w$  value. Excretion of phosphatases occurs in response to P deficiency in the plant. It is therefore questionable how important phosphatases can be if we want to avoid P deficiencies in the crop.

### Conclusion

Our mechanistic model cannot replace field experiments as a basis for a P-recommendation scheme. The approach chosen, however, has a number of clear advantages, which make further development and validation desirable:

- in our scheme, recommendations can be refined for different yield levels or crop varieties once a few simple crop parameters are known,
- for new crops or growing conditions recommendations can be made with a reduced research effort (a few intensively quantified rather than many extensively quantified field experiments), especially when the parameters required are known from other research,
- effects of modifications in the water balance of the soil can be predicted from our scheme to give recommendations that are more site-specific,
- field experiments can be used for rigorous testing of quantitative hypotheses rather than for parameter estimation as a basis of ad hoc adaptations of a qualitative theory about plant-soil fertility interactions.

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## **Chemical composition of animal manure: a modelling approach**

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### **Abstract**

A chemical equilibrium program (CHARON) was used to predict the chemical composition of the liquid fraction and the mineral fraction of pig and poultry manure. The results showed that the major part of calcium and magnesium in solution is complexed by dissolved organic matter. A large part of the dissolved organic matter is complexed with ammonium and potassium ions. Calculated ion activity products showed that possible mineral phases include vaterite, whitlockite, monetite and struvite in all the samples, and potassium taranakite in the pig manure samples. A number of other minerals are either unsaturated or so strongly supersaturated (e.g. apatite), that they do not control the solubility of major cations and anions. Scanning Electron Microscopy/Microprobe analysis showed the abundant presence of a magnesium phosphate, most likely the mineral struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) in one of the pig manure samples.

*Keywords:* animal manure, speciation, minerals, phosphate, chemical model

### **Introduction**

Animal manure is applied to agricultural land on a very large scale in the Netherlands. This has caused a number of environmental problems as discussed elsewhere (Japenga & Harmsen, 1990). Describing and understanding the chemical composition of manure and its various solid phases is prerequisite to understanding its environmental impact. In addition, the significance of nutrients in animal manure for plant growth is not yet completely understood. The as yet unexplained slow response of plants to phosphorus from animal manure during the first few weeks after application is just one example (Prummel & Sissingh, 1983).

We have used the detailed chemical analysis of three manure samples (Japenga & Harmsen, 1990) to construct a chemical model. Ion activity products (IAP) were used to determine the possible existence of mineral phases. Close agreement between an IAP value and the solubility product and correct prediction of the dissolved speciation provides strong circumstantial evidence for the occurrence of a particular mineral phase (e.g., calcium carbonate, phosphate minerals, etc.). To test these predictions we performed SEM/Microprobe analysis of the solid fraction of manure.

## Materials and methods

### *Manure composition*

The analytical procedures, and the data which are used in this article, were described by Japenga & Harmsen (1990). The data used in this article concern the samples PS-1, PM and PS-1/18. Some characteristics of these samples are given in Table 1. Sample PS-2 is not used in this article because too many essential data were missing. The solid fraction of PS-1/18 was examined for mineral composition by Scanning Electron Microscopy (SEM)/Microprobe (Philips 535, using 15 kV accelerating voltage). The slurry was centrifuged at high speed (18 000 rpm). The centrifuge residue was washed once with acetone, then dried at 35 °C overnight.

### *The chemical equilibrium program*

The chemical equilibrium program, which is used in this study, solves the chemical equilibrium problem by minimizing the Gibbs free energy (GFE) of the equilibrium system while keeping the mass balance constraints. The equilibrium program was developed at the RAND corporation (Shapiro, 1964; Clasen, 1965; Shapley et al., 1968). The algorithms which are used, a first-order gradient projection method and the second-order RAND algorithm, are described by Clasen (1965) and by Smith & Missen (1982). The version of the program used in this study was developed at the Delft Hydraulics Laboratory (de Rooij, 1988) and is an integral part of the chemical program CHARON.

### *Formulations used in the equilibrium program*

To calculate equilibrium, a GFE parameter has to be attributed to each species of the equilibrium system. CHARON needs dimensionless GFE parameters. The standard unit of the GFE in thermodynamics is kcal mol<sup>-1</sup> (or kJ mol<sup>-1</sup>). These values are converted to dimensionless parameters by dividing the values by the product of the gas constant  $R$  (1.98717 cal mol<sup>-1</sup> K<sup>-1</sup>) and the absolute temperature at the standard state (298.15 K).

CHARON uses the Raoult convention for the concentration unit. This means that all concentrations are expressed as moles per total number of moles in a certain phase (the mole fraction). In chemistry, the standard state of a substance dissolved

Table 1. Relevant characteristics of the slurry samples.

Sample	Type	Age (months)	Characterization
PS-1	pig manure	2-4	low total solids, high ammonium
PS-1/18	pig manure	20-22	same sample as PS-1, but stored at 4 °C for 18 months
PM	poultry manure	2-4	high calcium carbonate content

## CHEMICAL COMPOSITION OF ANIMAL MANURE

Table 2. Conversion of standard GFE data to C-parameters.

Phase	Species	$\Delta G_f^\circ$ (kcal mol <sup>-1</sup> )	Henry Raoult	$\Delta G_f^\circ/RT$ (Raoult)	C-parameter (-)
Water	H <sup>+</sup>	0.0	4.017	4.017	0.0
	OH <sup>-</sup>	-37.594	4.017	-59.436	0.0
	H <sub>2</sub> O	-56.687	0.0	-95.678	-40.259
	H <sub>2</sub> CO <sub>3</sub>	-148.95	4.017	-247.387	-46.465
	HCO <sub>3</sub> <sup>-</sup>	-140.27	4.017	-232.736	-27.798
	CO <sub>3</sub> <sup>--</sup>	-126.18	4.017	-208.955	0.0
	Ca <sup>++</sup>	-132.52	4.017	-219.655	0.0
	CaOH <sup>+</sup>	-171.89	4.017	-286.106	-7.014
	CaHCO <sub>3</sub> <sup>+</sup>	-274.33	4.017	-459.007	-34.414
	CaCO <sub>3</sub>	-263.00	4.017	-439.884	-11.274
	Calcite	CaCO <sub>3</sub> S	-270.18	0.0	-456.019
CO <sub>2</sub> gas	CO <sub>2</sub>	-94.26	0.0	-159.095	-13.593

in water is defined for the hypothetical state of infinite dilution, and at the same time a molality of 1 (the Henry convention).

Since CHARON uses the Raoult convention, values of GFE which are tabulated for the Henry convention, have to be transformed. This is done by adding to the value of  $\Delta G_f^\circ/RT$  the value of the natural logarithm of 55.51 (1 kg water is 55.51 moles water). A last transformation which is often applied to the GFE parameters for CHARON calculations is the transformation to other zero-points. In standard thermodynamics, the zero-points of the GFE are given to the elements of the periodic system. However, this choice is arbitrary, since GFE values are relative quantities. To get a more convenient set of GFE parameters, the zero-points are chosen differently, depending on the problem. The GFE parameters in CHARON are called C-parameters. As an example of the calculation of C-parameters from  $\Delta G_f^\circ$  values Table 2 shows the transformations for the system H<sub>2</sub>O — CaCO<sub>3</sub> — CO<sub>2</sub> (gas). In this example the species H<sup>+</sup>, OH<sup>-</sup>, Ca<sup>++</sup> and CO<sub>3</sub><sup>--</sup> get a zero value for the GFE parameter ( $\Delta G_f^\circ$  data taken from Sadiq & Lindsay, 1979).

## Modelling manure

### Model definition

The manure liquid is modelled according to the system definition supplied in appendix A. The C-parameter is defined to be zero for the species H<sup>+</sup>, OH<sup>-</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>--</sup>, PO<sub>4</sub><sup>----</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Mn<sup>++</sup>, Fe<sup>++</sup>, Al<sup>+++</sup>. The organic complexing capacity is represented by the component FAAC (fatty acids). The species FAAC, which represents the 'free' complexing sites, is assigned the value zero for the C-parameter. In appendix A for each species the  $\Delta G_f^\circ$  and its source are provided.

Data on a number of possibly important complexes could not be found in the literature. Especially data on major complexes of  $\text{NH}_4^+$  (with  $\text{Cl}$ ,  $\text{CO}_3$ ,  $\text{HCO}_3$ ,  $\text{HPO}_4$ ) are lacking. It is important to know the values of association constants of these complexes because  $\text{NH}_4^+$  is the cation at the highest concentration in manure liquid (Japenga & Harmsen, 1990). Thus, interactions between ammonium and ligands will have a profound influence on the activity of the ligands. Therefore, we determined experimentally the association constants of ammonium acetate ( $\text{NH}_4\text{AC}$ ), ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) and potassium chloride ( $\text{KCl}$ ) ionpairs, by measuring the conductivity of salt solutions having different concentrations. Potassium chloride was taken as a reference, since the ionpair formation constant for this salt is available from the literature. Sadiq & Lindsay (1979) reported an association constant for this ionpair of 0.2, after measurements of Paterson et al. (1971). Garrels & Christ (1965) reported an association constant of 1.0. The value we found is  $0.3 \pm 0.05$ , which agrees quite well with the value reported by Sadiq & Lindsay.

The constants which were determined, and the ammonium sulphate association constant (Truesdell & Jones, 1974), were used to fit values for other ionpairs based on the known values of the equivalent potassium and hydrogenium ( $\text{H}^+$ ) ionpairs. It is assumed that the ammonium ion has ionic properties comparable to those of the potassium ion, but is able to interact more strongly with proton acceptors (the ammonium ion is a weak acid).

For missing potassium or sodium ionpairs, the stability constants were calculated from a regression of available data (Sadiq & Lindsay, 1979; Turner et al., 1981; Sposito & Mattigod, 1980) for both ions.

The organic complexation constants of the  $1^+$  cations are defined as equal to the carbonate stability constants. Since very few data are available on the stability of organic complexes of  $1^+$  cations, and since for  $2^+$  cations the relation

$$\log(\text{K-humic}) = 0.5 + \log(\text{K-CO}_3^{--})$$

can be used (data of Mantoura et al. (1978) for the values of the humic complexes compared with carbonate complexing constants given by Turner et al., 1981), this assumption probably does not overestimate the stability of the organic complexation of the  $1^+$  cations. The values used in this study are listed in Table 3. The stability of the  $\text{Al}^{+++}$ -phosphate complexes were estimated using the stability of the appropriate  $\text{Fe}^{+++}$  complexes and the difference in stability between the solids variscite and strengite.

Other stability constants, with the exception of the values for the FAAC-complexes, were mainly taken from Sadiq & Lindsay (1979). However, if Sadiq & Lindsay did not provide a value for a possibly important species, other literature sources were used (Turner et al., 1981; Sposito & Mattigod, 1980).

The liquid fraction of manure contains a large amount of dissolved organic substances. These substances influence the activity of dissolved cations by forming complexes. The formation constant of such a complex is often referred to as being conditional, which means that it is only applicable to the system under consideration

Table 3. Estimated  $\Delta G_f^\circ$  values and C-parameters of 1+ cation complexes.

	K <sup>+</sup>	C-K <sup>+</sup>	Na <sup>+</sup>	C-Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	C-NH <sub>4</sub> <sup>+</sup>
Free ion	-67.51	0.0	-62.59	0.0	-18.99	0.0
Cl <sup>-</sup>	-98.17	-2.81	-93.14	-2.64	-49.66	-2.85
CO <sub>3</sub> <sup>--</sup>	-194.92	-6.09	-190.50	-6.94	-147.08	-7.22
HCO <sub>3</sub> <sup>-</sup>	-207.61	-31.52	-203.20	-32.39	-159.50	-32.22
FAAC <sup>a</sup>	-68.74	-6.09	-64.32	-6.94	-20.89	-7.22
PO <sub>4</sub> <sup>---</sup>	-315.28	-8.39	-310.41	-8.47	-267.36	-9.50
HPO <sub>4</sub> <sup>--</sup>	-331.11	-39.12	-326.21	-39.15	-283.13	-40.02
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-339.29	-56.95	-334.70	-57.50	-291.38	-57.98

<sup>a</sup>  $\Delta G_f^\circ$  of FAAC defined as zero.

(because it depends heavily on the type and amount of organics present). Since measured stability constants of the organic complexes were not available, the stability constants were estimated.

If it is assumed that the concentration of carboxylic groups (referred to as 'fatty acids'), which is determined by titration (Japenga & Harmsen, 1990), represents the total number of dissolved organic complexation sites, and furthermore equilibrium with calcium carbonate with a solubility product of  $10^{-7.6}$  is assumed, then the stability constant of the organic complexation of the calcium ion can be calculated from the measured calcium concentration, the pH and the alkalinity. The result is a stability constant of  $10^{2.87}$  for sample PS-1,  $10^{3.05}$  for sample PM and  $10^{3.38}$  for sample PS-1/8. The value of this constant seems to increase with ageing of the manure. The literature values for the conditional equilibrium constants for humic complexes of calcium are in the order of  $10^{3.2}$  to  $10^{4.6}$  at pH = 8.0 (Mantoura et al., 1978). The pH of the manure liquid is between 7.5 and 8. The calculated values are in good agreement with these literature data.

Using  $10^3$  as the calcium complexation constant, the stability constant of the magnesium complex can be estimated to be about  $10^{2.5}$ . The complex constants for the Fe<sup>++</sup> and Mn<sup>++</sup> organic complexes are both estimated to be  $10^{4.5}$ . The stability of the Al<sup>+++</sup> complex is estimated to be  $10^9$ , the constant of Fe<sup>+++</sup>  $10^{14}$ .

## Results

### *Complexation of the major cations*

Tables 4 and 5 show the calculated speciation of the manure liquid phase. It shows that for instance for calcium in the sample PS-1, although the dissolved concentration is  $170 \text{ mg l}^{-1}$  (Japenga & Harmsen, 1989), the free calcium ion only has a concentration of 10.2 % of this value ( $17.3 \text{ mg l}^{-1}$ ). Together with an activity coefficient of 0.25 (ionic strength is 0.45), this means that the activity of calcium in the manure liquid is only 2.5 % of the dissolved calcium concentration.

In Table 4 the calculated percentage distribution of the cations over the different ligands in the manure liquid phase, and in Table 5 the calculated percentage distri-

Table 4. Percentage distribution of cations over various ligands in the manure liquid.

Cation	Free	Ligands					
		Cl <sup>-</sup>	OH <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>--</sup>	ΣPO <sub>4</sub>	FAAC
<i>(a) Sample PS-1</i>							
Ca <sup>++</sup>	10.2	0.1	— <sup>a</sup>	9.5	1.1	0.3	78.8
Mg <sup>++</sup>	8.6	0.1	—	8.5	1.4	0.5	80.8
K <sup>+</sup>	75.5	0.7	—	10.0	0.2	0.2	13.4
Na <sup>+</sup>	59.4	0.5	—	11.5	0.3	0.2	28.1
NH <sub>4</sub> <sup>+</sup>	52.8	0.6	0.7	12.2	0.2	0.2	33.3
Mn <sup>++</sup>	0.2	—	—	39.3	0.4	—	60.1
Fe <sup>++</sup>	0.1	—	—	3.0	1.4	—	95.5
Al <sup>+++</sup>	—	—	13.8	—	0.1	—	86.1
<i>(b) Sample PS-1/18</i>							
Ca <sup>++</sup>	12.2	0.1	—	15.0	3.3	0.5	68.9
Mg <sup>++</sup>	10.2	0.1	—	13.5	4.2	0.8	71.2
K <sup>+</sup>	81.0	0.7	—	14.2	0.4	0.2	3.4
Na <sup>+</sup>	71.7	0.5	—	18.5	1.0	0.2	8.0
NH <sub>4</sub> <sup>+</sup>	66.4	0.6	1.6	20.4	0.8	0.3	9.8
Mn <sup>++</sup>	0.2	—	—	77.9	1.5	—	20.4
Fe <sup>++</sup>	0.3	—	—	13.5	11.9	0.1	74.1
Al <sup>+++</sup>	—	—	84.2	—	0.2	—	15.6
<i>(c) Sample PM</i>							
Ca <sup>++</sup>	8.0	0.1	—	5.7	0.6	0.45	85.2
Mg <sup>++</sup>	6.8	0.1	—	5.0	0.7	0.7	86.7
K <sup>+</sup>	78.5	0.9	—	7.9	0.1	0.3	12.3
Na <sup>+</sup>	63.3	0.6	—	9.3	0.2	0.3	26.3
NH <sub>4</sub> <sup>+</sup>	56.8	0.7	0.6	9.9	0.2	0.4	31.4
Mn <sup>++</sup>	0.2	—	—	35.1	0.3	—	64.3
Fe <sup>++</sup>	0.1	—	—	2.5	1.0	—	96.3
Al <sup>+++</sup>	—	—	8.3	—	0.1	—	91.6

<sup>a</sup> — is < 0.1 % or not modelled.

bution of the anions over the different cations in the liquid phase is shown. Tables 4 and 5 show that the major part of Ca<sup>++</sup> and Mg<sup>++</sup> are complexed by the ligand FAAC, whereas the larger part of FAAC forms complexes with NH<sub>4</sub><sup>+</sup> and K<sup>+</sup>. Since the activity of calcium and magnesium determines to a large extent the possible mineral phases in the manure solid, it is clear that the organic complexation of these ions is the major controlling factor in determining the composition of the inorganic solids. This complexation is influenced strongly by the concentration of ammonium and potassium.

The activity of the phosphate ion, which is also of great importance for the inorganic solid composition, is also strongly influenced by the ammonium and potassi-

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Table 5. Percentage distribution of ligands over various cations in the manure liquid.

Ligands	Free	Cations						Speciation free
		Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	rest	
<i>(a) Sample PS-1</i>								
Cl <sup>-</sup>	95.7	-	-	0.1	1.4	2.8	-	
C-inorg	*	0.1	-	1.0	5.0	16.0	0.1	* CO <sub>2</sub> 3.1, HCO <sub>3</sub> <sup>-</sup> 74.3, CO <sub>3</sub> <sup>--</sup> 0.4
FAAC	17.5	1.7	0.4	3.5	10.3	66.4	0.2	
ΣPO <sub>4</sub>	*	0.6	0.2	1.9	10.9	42.2	-	* H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> 6.5, HPO <sub>4</sub> <sup>--</sup> 37.7
<i>(b) Sample PS-1/18</i>								
Cl <sup>-</sup>	95.2	-	-	0.2	1.4	3.2	-	
C-inorg	*	0.1	-	1.1	5.0	18.5	0.1	* CO <sub>2</sub> 1.5, HCO <sub>3</sub> <sup>-</sup> 73.0, CO <sub>3</sub> <sup>--</sup> 0.7
FAAC	15.2	1.8	0.5	3.8	9.3	69.2	0.2	
ΣPO <sub>4</sub>	*	0.2	0.1	2.2	10.6	45.4	-	* H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> 3.2, HPO <sub>4</sub> <sup>--</sup> 38.3
<i>(c) Sample PM</i>								
Cl <sup>-</sup>	96.2	-	-	0.2	1.9	1.7	-	
C-inorg.	*	0.2	-	1.4	6.9	9.9	0.1	* CO <sub>2</sub> 4.2, HCO <sub>3</sub> <sup>-</sup> 77.0, CO <sub>3</sub> <sup>--</sup> 0.3
FAAC	22.0	4.7	0.8	6.2	16.9	49.1	0.3	
ΣPO <sub>4</sub>	*	1.1	0.3	3.1	16.3	29.2	-	* H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> 9.3, HPO <sub>4</sub> <sup>--</sup> 40.7

um concentration (45-55 % of the total dissolved phosphate is bound in ammonium and potassium ionpairs).

*Ion activity products for mineral phases*

To evaluate the possible inorganic solids in equilibrium with manure liquid, activity product calculations can be performed for the liquid phase. Solids in equilibrium with the liquid should have an activity product close to the literature value of the solubility product.

The theoretical solubility product for the solid A<sub>n</sub>B<sub>m</sub> is defined as:

$$K_{sp} = a_A^n \times a_B^m$$

where:

a<sub>A</sub> = the activity of the dissolved species A

a<sub>B</sub> = the activity of the dissolved species B

Values of K<sub>sp</sub> have been tabulated in the thermodynamic literature.

Mineral equilibrium data used in this study were taken from the work of Sadiq & Lindsay (1979) (all data except vaterite, since no value is supplied for this mineral) and Plummer & Busenberg (1982) (vaterite).

The calculated ion activity product in the liquid fraction of manure is now defined as:

$$\text{IAP} = a_{\text{A}}^n \times a_{\text{B}}^m$$

A measure of the degree of saturation of a solid is the value of IAP/Ksp for this solid.

Even in the presence of reactive solid phases, differences between theoretical solubility products and ion activity products can occur for a number of reasons, e.g.:

1) When solids precipitate, some degree of supersaturation occurs. Supersaturation in itself is required for nucleation of new crystals, and supersaturation will remain when precipitation is relatively fast.

2) When solids dissolve, some undersaturation is necessary to keep the dissolution going.

3) Not only the ion activity products but also the kinetics of precipitation determine to a large extent the possible solid mineral phases. Some minerals are precipitating so slowly that formation can occur only over very long periods of time. As a rule, minerals with a simple molecular structure precipitate faster than minerals with a complex molecular structure. Other ions than the constituent ions may influence the kinetics. For instance, magnesium ions may influence the precipitation kinetics of calcium phosphates; especially the precipitation of  $\beta$ -TCP is enhanced (Lindsay & Vlek, 1977).

4) Theoretical solubility products are determined on pure, highly crystalline solids. In manure, the mineral phases will seldom be absolutely pure solids since various cations and anions may replace the main constituent ions (solid solution). Also, the crystallinity may vary depending on the rate of precipitation.

So there is a range of IAP values around the theoretical solubility product where neither precipitation nor dissolution occurs. However, the larger the difference between IAP and Ksp, the lower the probability of equilibrium between a certain solid phase and the liquid. Table 6 lists the results of the ion activity calculations for the liquid phase of manure.

The calculated IAP values show that possible mineral phases (with  $\log(\text{IAP}/\text{Ksp})$  between  $-1$  and  $+1$ ), which can be in equilibrium with the samples are:

1) Calcium carbonate. The IAP of calcium carbonate is closest to the saturation of vaterite (Plummer & Busenberg, 1982), a more soluble form than calcite. Magnesium carbonate probably does not form as a single solid, but as a solid solution in the vaterite.

2) Whitlockite ( $\beta$ -tricalciumphosphate) and/or monetite ( $\text{CaHPO}_4$ ).

3) Struvite. This mineral, a magnesium-ammonium-phosphate, has been identified in the solid fraction of manure samples by X-ray diffraction (Fordham & Schwertmann, 1977). The fact that it shows a slight undersaturation is probably due to the assumptions made about the complexing capacity of the manure liquid.

4) K-taranakite in the pig manure samples,  $\text{NH}_4$ -taranakite in the poultry sample.

5) Possible other precipitates are: aluminum hydroxide (amorphous), manganese phosphate ( $\text{MnHPO}_4$ ), siderite ( $\text{FeCO}_3$ ).

With respect to other minerals, the manure is either unsaturated, or so strongly supersaturated (e.g. apatite), that even if present, they do not control the solubility of the major cations and anions.

Table 6.  $\Delta G_f^\circ$  of minerals and  $\log(\text{IAP}/\text{Ksp})$  of the liquid phase of manure.

Formula and mineral name	$\Delta G_f^\circ$ (kcal mol <sup>-1</sup> )	$\log(\text{IAP}/\text{Ksp})$		
		PM	PS-1	PS-1/18
Al(OH) <sub>3</sub> (amorphous)	-274.21	0.53*	0.56*	1.26
Al(OH) <sub>3</sub> (gibbsite)	-276.43	2.16	2.19	2.89
AlPO <sub>4</sub> (berlinite)	388.50	-1.53	-1.88	-1.73
AlPO <sub>4</sub> ·2H <sub>2</sub> O (varescite)	-505.97	1.46	1.10	1.26
H <sub>6</sub> K <sub>3</sub> Al <sub>5</sub> (PO <sub>4</sub> ) <sub>8</sub> ·18H <sub>2</sub> O (K-taranakite)	-4014.76	2.74	-0.23*	-0.19*
H <sub>6</sub> (NH <sub>4</sub> ) <sub>3</sub> Al <sub>5</sub> (PO <sub>4</sub> ) <sub>8</sub> ·18H <sub>2</sub> O (NH <sub>4</sub> -taranakite)	-3864.84	-0.65*	-2.58	-2.35
CaCO <sub>3</sub> (aragonite)	-269.87	0.70*	0.77*	0.76*
CaCO <sub>3</sub> (calcite)	-270.18	0.93*	1.0	0.99*
CaCO <sub>3</sub> (vaterite)	-269.26	0.25*	0.32*	0.31*
CaCO <sub>3</sub> ·6H <sub>2</sub> O (ikaite)	-607.52	-1.11	-1.05	-1.05
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O (MCP)	-734.48	-9.92	-10.65	-11.60
CaHPO <sub>4</sub> ·2H <sub>2</sub> O (brushite)	-516.89	-0.68*	-1.03	-1.43
CaHPO <sub>4</sub> (monetite)	-403.96	-0.33*	-0.68*	-1.09
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (α-TCP)	-922.70	-2.46	-3.16	-3.80
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (whitlockite, β-TCP)	-927.37	0.97*	0.30*	-0.38*
Ca <sub>8</sub> H <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> ·5H <sub>2</sub> O (OCP)	-2942.62	-1.30	-3.35	-5.51
Ca <sub>10</sub> (OH) <sub>2</sub> (PO <sub>4</sub> ) <sub>6</sub> (hydroxyapatite)	-3030.24	15.76	13.77	11.87
MgCO <sub>3</sub> (magnesite)	-245.37	-0.76*	-0.58*	-0.51*
MgCO <sub>3</sub> ·3H <sub>2</sub> O (nesquehonite)	-411.62	-3.56	-3.4	-3.32
MgCa(CO <sub>3</sub> ) <sub>2</sub> (dolomite)	-518.25	2.15	2.4	2.46
Mg(OH) <sub>2</sub> (brucite)	-199.41	-6.36	-6.23	-6.01
MgHPO <sub>4</sub> ·3H <sub>2</sub> O (newberryite)	-549.04	-2.15	-2.40	-2.73
MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O (struvite)	-731.24	-0.76*	-0.69*	-0.67*
MgKPO <sub>4</sub> ·6H <sub>2</sub> O	-776.31	-3.23	-3.50	-3.53
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O (boberrite)	-1304.99	-5.16	-5.55	-5.99
Mn(OH) <sub>2</sub> (pyrochroite)	-147.76	-8.38	-8.22	-7.95
MnCO <sub>3</sub> (rhodochroisite)	-195.03	-1.81	-1.61	-1.48
MnHPO <sub>4</sub>	-334.79	1.32	1.09	0.82*
Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	-692.96	-13.81	-14.09	-14.37
FeCO <sub>3</sub> (siderite)	-161.95	-1.01	-1.40	-0.29*
Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·8H <sub>2</sub> O (vivianite)	-1058.36	-3.29	-5.34	-2.69
Fe(OH) <sub>3</sub> (amorphous)	-169.25	-7.15	-6.93	-6.46
FeOOH (goethite)	-117.42	-3.59	-3.36	-2.89
FePO <sub>4</sub>	-283.19	-9.47	-9.63	-9.70
FePO <sub>4</sub> ·2H <sub>2</sub> O (strengite)	-398.59	-8.00	-8.16	-8.23

\* Possible mineral phase (-1 < log(IAP/Ksp) < 1).

*Solid phase analysis using Scanning Electron Microscopy*

To verify the model predictions, we performed SEM/Microprobe analysis on the solid fraction of sample PS-1/18.

Fig. 1 shows an EM picture of the solid fraction of sample PS-1/18. It was found to contain large (5-35  $\mu\text{m}$  size) prismatic crystals (crystal A in Fig. 1). Upon examination of the microprobe X-ray spectrum (Fig. 2) the crystals were found to contain magnesium and phosphorus, and a small amount of potassium. Both the crystal habitus and the elemental composition strongly suggest the presence of struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ). Potassium occurs through substitution for ammonium.

Some particles (size about 5-10  $\mu\text{m}$  length) containing calcium and phosphorus were also found (e.g. crystal C in Fig. 1). The mineral form of this calcium phosphate could not be established. Since these particles were only detected after careful examination of the element map pictures (e.g. Fig. 10), no X-ray spectrum is available. Phosphorus was not detected in large quantities in other mineral particles.

Many flaky, possibly amorphous aggregates were detected, and found to contain

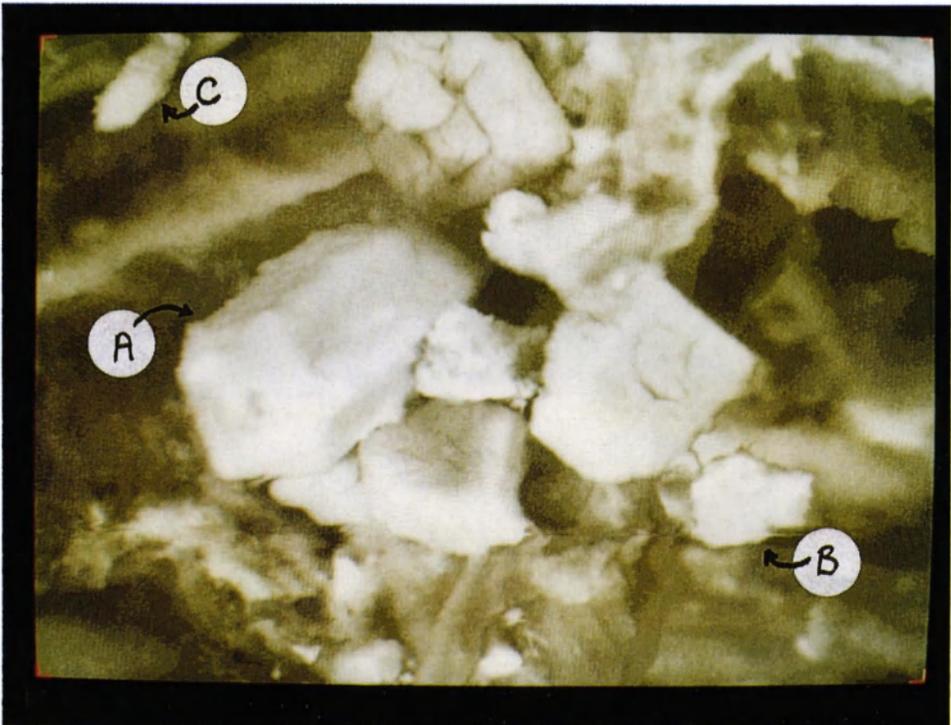


Fig. 1. EM picture of solid fraction of sample PS-1/18. A and B, respectively, denote crystals of which X-ray spectra are shown in Figs. 3 and 4. Crystal C is a calcium phosphate.

calcium and carbon (crystal B in Fig. 1, X-ray spectrum in Fig. 3), suggesting that the aggregates are some form of calcium carbonate ( $\text{CaCO}_3$ , vaterite?). The microprobe X-ray spectrum of this mineral shows a low magnesium concentration, indicating little coprecipitation of magnesium with calcium. Other particles had high concentrations of aluminum and silicon, but no elevated phosphorus content. Thus

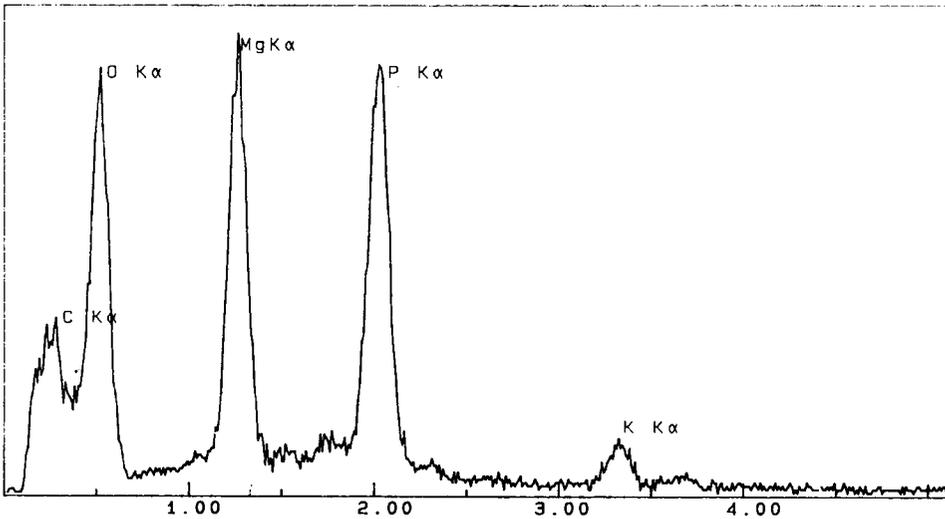


Fig. 2. X-ray spectrum of crystal A (probably struvite).

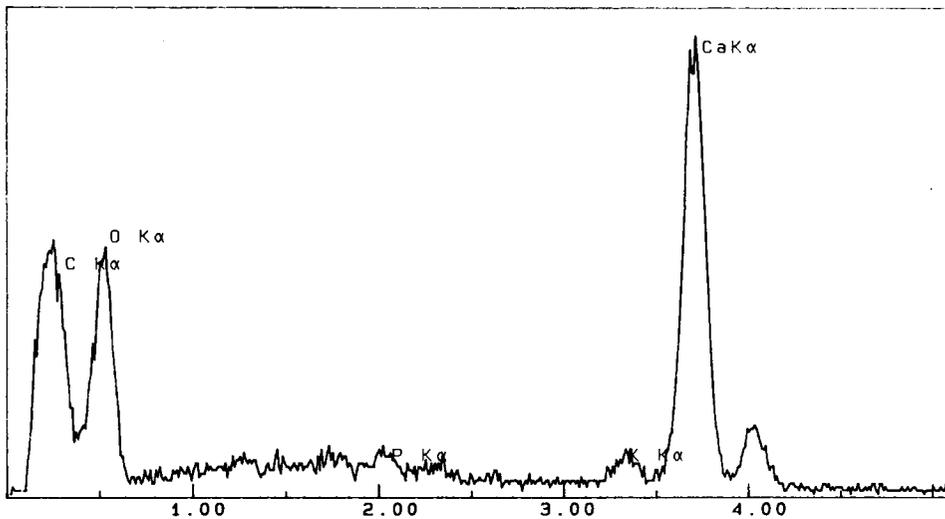


Fig. 3. X-ray spectrum of crystal B (probably vaterite).

these particles were not taranakite but probably a clay mineral (Fig. 4). One silica crystal, probably quartz (Fig. 5), was found.

Calcium and potassium were found to be related to the organic matrix (Fig. 6). Furthermore it was found that the composition of the organic material was very variable with respect to sulfur, potassium, phosphorus and major cations (Fig. 7,

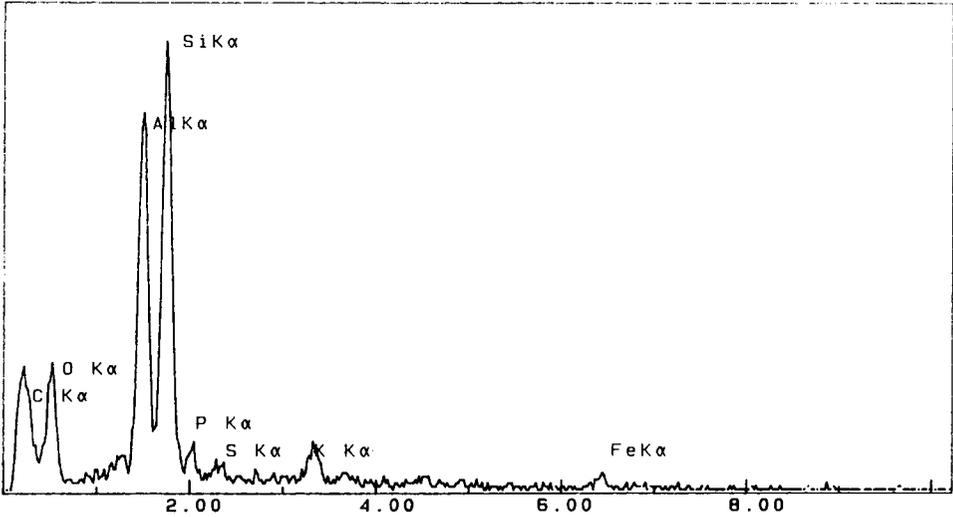


Fig. 4. X-ray spectrum of a clay mineral.

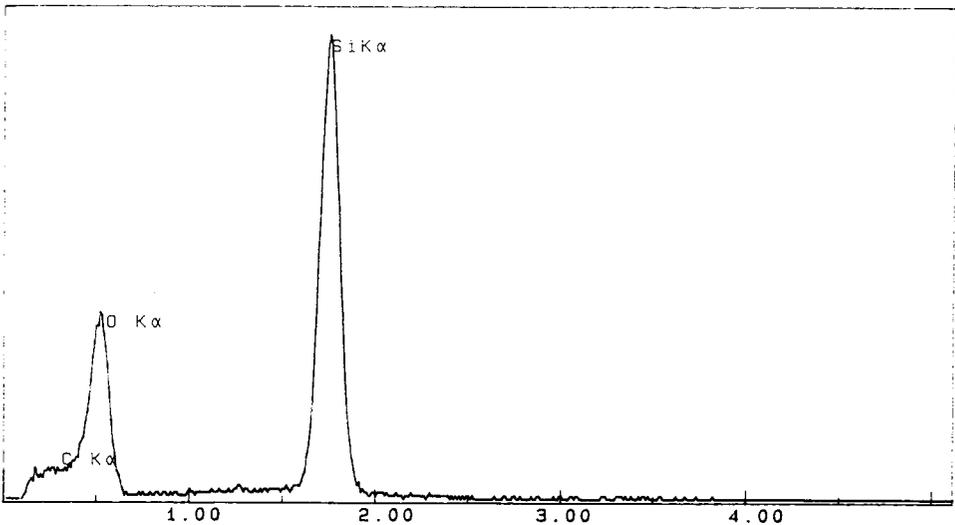


Fig. 5. X-ray spectrum of silica crystal (probably quartz).

compare Fig. 6).

X-ray element maps (Figs. 8 (P), 9 (Mg), 10 (Ca and P) and 11 (Ca and Mg)) show that the major part of the phosphorus and magnesium is bound within the magnesium phosphate crystals (struvite), making this by far the most abundant mineral phase in the solid fraction of the manure.

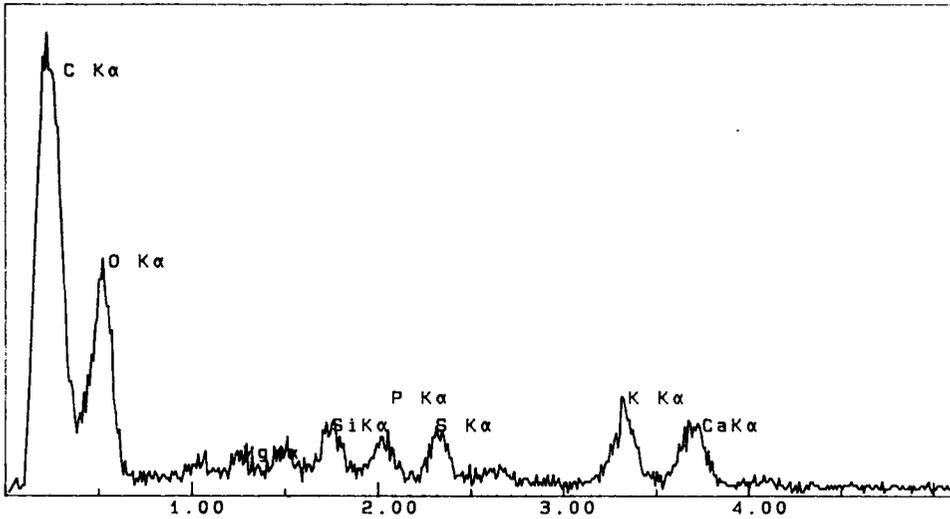


Fig. 6. X-ray spectrum of organic matter.

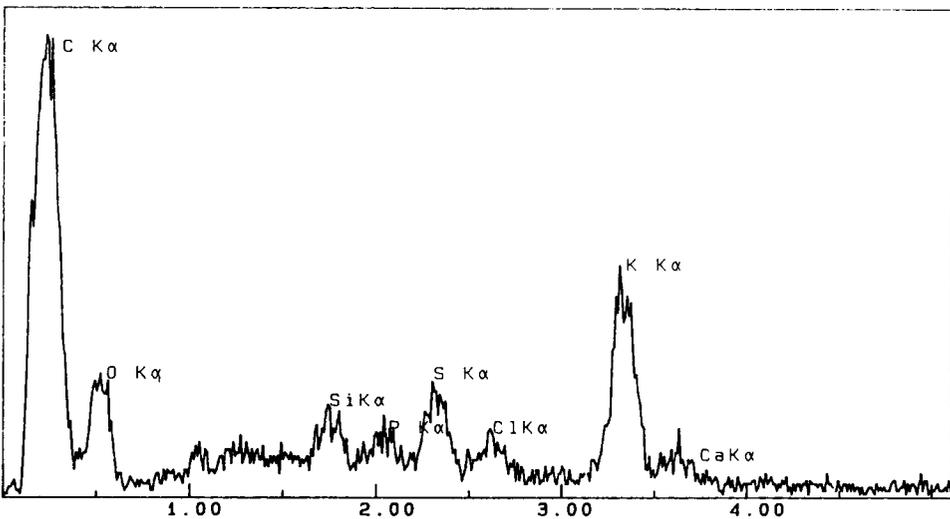


Fig. 7. X-ray spectrum of organic matter. Note the difference in composition from spectrum in Fig. 6.



Fig. 8. X-ray element map of phosphorus from the same area as shown in Fig. 2.



Fig. 9. X-ray element map of magnesium from the same area as shown in Fig. 2.

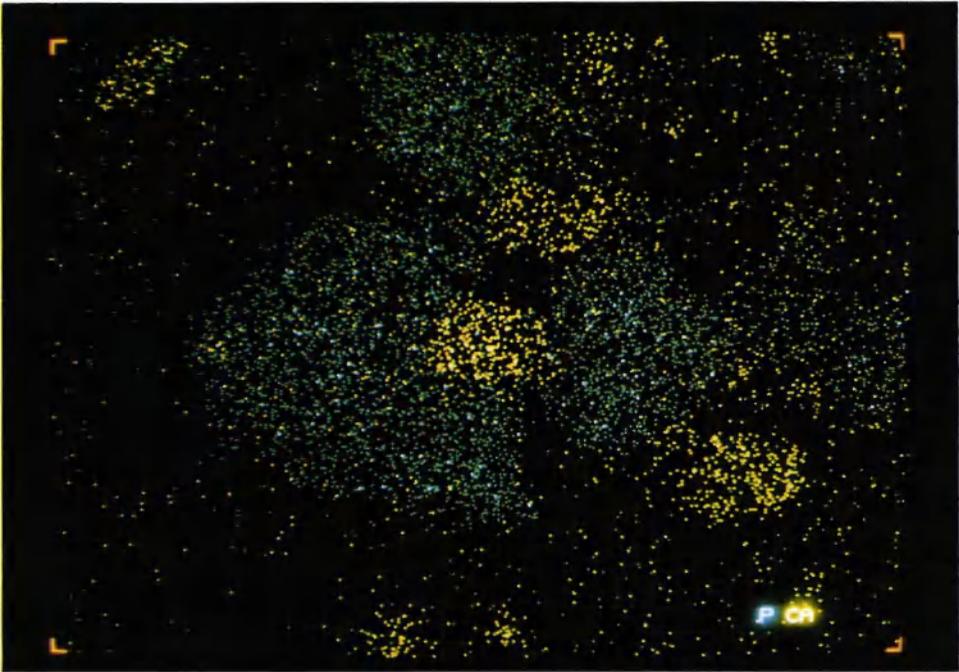


Fig. 10. X-ray element map of calcium (yellow) and phosphorus (green) from the same area as shown in Fig. 2.

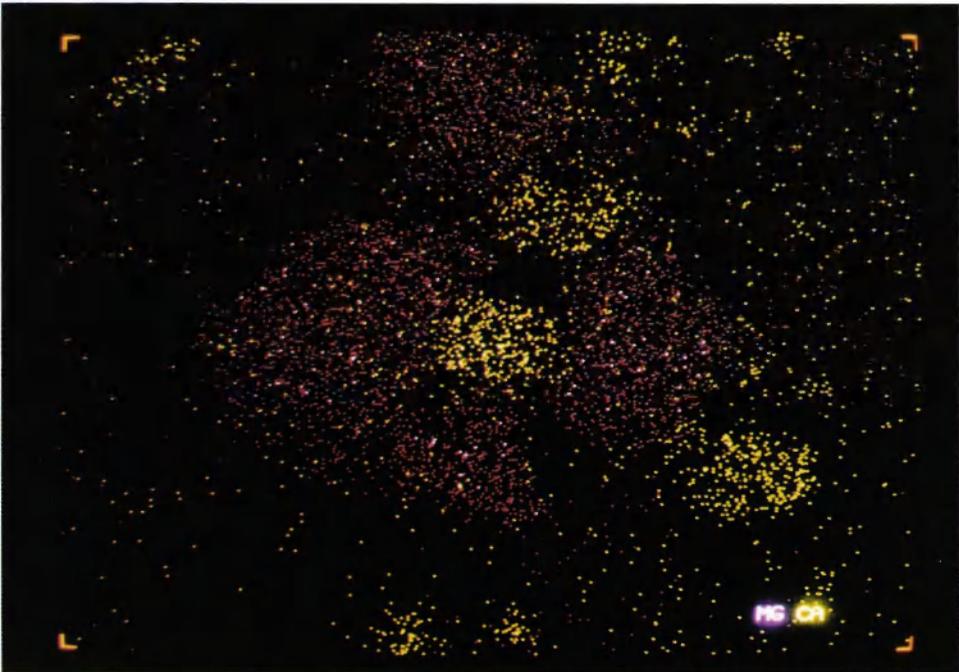


Fig. 11. X-ray element map of calcium (yellow) and magnesium (red) from the same area as shown in Fig. 2.

## Discussion

The results of the chemical model calculations and the SEM/Microprobe analysis both show the importance of the mineral struvite in determining the phosphate concentration in the manure liquid phase. One of the reasons for the slow response of plants to animal manure phosphate is probably the slow dissolution of this mineral. This, however, has to be verified by experiments. The calculations show the importance of the dissolved organic substances in the manure liquid. Too little information is presently available on complexation capacity and strength of these substances. These substances probably also play a major role in the initial stages of the interaction of animal manure with the soil system. To understand this interaction, more study is necessary.

The model which is described in this article can be used to study the interactions between manure and soil. The model can also be used to study the effects of acidification of animal manure (a treatment proposed in the Netherlands to reduce volatilization of ammonia) on the composition of the manure.

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Appendix A

System definition manure liquid phase as used as input for CHARON.

Species name	$\Delta G_f^\circ$ (kcal mol <sup>-1</sup> )	Ref.	C-param.	Stoichiometry (components)			
H <sup>+</sup>	0.0	1	0.0	1 H <sup>+</sup>			
OH <sup>-</sup>	-37.59	1	0.0	1 OH <sup>-</sup>			
H <sub>2</sub> O	-56.69	1	-40.26	1 OH <sup>-</sup>	1 H <sup>+</sup>		
O <sub>2</sub>	3.9	1	137.51	2 OH <sup>-</sup>	-2 H <sup>+</sup>		-4 EL <sup>-</sup>
Cl <sup>-</sup>	-31.37	1	0.0	1 Cl <sup>-</sup>			
CO <sub>2</sub>	-92.26	1	-6.21	1 CO <sub>2</sub>			
HCO <sub>3</sub> <sup>-</sup>	-140.27	1	-27.80	1 CO <sub>2</sub>	1 OH <sup>-</sup>		
CO <sub>3</sub> <sup>--</sup>	-126.18	1	0.0	1 CO <sub>2</sub>	1 OH <sup>-</sup>		-1 H <sup>+</sup>
FAAC	0.0	D	0.0	1 FAAC			
PO <sub>4</sub> <sup>---</sup>	-245.18	1	0.0	1 PO <sub>4</sub> <sup>---</sup>			
HPO <sub>4</sub> <sup>--</sup>	-262.03	1	-32.46	1 PO <sub>4</sub> <sup>---</sup>	1 H <sup>+</sup>		
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-271.85	1	-53.30	1 PO <sub>4</sub> <sup>---</sup>	2 H <sup>+</sup>		
Al <sup>+++</sup>	-117.33	1	0.0	1 Al <sup>+++</sup>			
AlCO <sub>3</sub>	-255.01	2	-23.43	1 Al <sup>+++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
AlHCO <sub>3</sub>	-260.84	3	-37.98	1 Al <sup>+++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
AlPO <sub>4</sub>	-373.15	E	-21.98	1 Al <sup>+++</sup>	1 PO <sub>4</sub> <sup>---</sup>		
AlHPO <sub>4</sub>	-389.14	E	-52.98	1 Al <sup>+++</sup>	1 PO <sub>4</sub> <sup>---</sup>	1 H <sup>+</sup>	
AlH <sub>2</sub> PO <sub>4</sub>	-393.49	E	-64.59	1 Al <sup>+++</sup>	1 PO <sub>4</sub> <sup>---</sup>	2 H <sup>+</sup>	
AlOH <sup>++</sup>	-167.17	1	-24.69	1 Al <sup>+++</sup>	1 OH <sup>-</sup>		
AlOH <sub>2</sub> <sup>+</sup>	-218.02	1	-51.08	1 Al <sup>+++</sup>	2 OH <sup>-</sup>		
AlOH <sub>3</sub>	-266.94	1	-74.21	1 Al <sup>+++</sup>	3 OH <sup>-</sup>		
AlOH <sub>4</sub> <sup>-</sup>	-312.25	1	-91.25	1 Al <sup>+++</sup>	4 OH <sup>-</sup>		
AlOH <sub>5</sub> <sup>--</sup>	-354.06	1	-102.40	1 Al <sup>+++</sup>	5 OH <sup>-</sup>		
AlFAAC	-129.61	E	-24.74	1 Al <sup>+++</sup>	1 FAAC		
Ca <sup>++</sup>	-132.54	1	0.0	1 Ca <sup>++</sup>			
CaCO <sub>3</sub>	-263.00	1	-11.27	1 Ca <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
CaHCO <sub>3</sub>	-274.33	1	-34.42	1 Ca <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
CaOH <sup>+</sup>	-171.89	1	-7.01	1 Ca <sup>++</sup>	1 OH <sup>-</sup>		

Appendix A continued.

Species name	$\Delta G_f^\circ$ (kcal mol <sup>-1</sup> )	Ref.	C-param.	Stoichiometry (components)			
CaCl <sup>+</sup>	-163.10	3	-2.64	1 Ca <sup>++</sup>	1 Cl <sup>-</sup>		
CaPO <sub>4</sub> <sup>-</sup>	-386.53	2	-18.89	1 Ca <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>		
CaHPO <sub>4</sub>	-398.29	1	-42.78	1 Ca <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>	
CaH <sub>2</sub> PO	-406.28	1	-60.56	1 Ca <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>	
CaFAAC	-136.63	E	-10.92	1 Ca <sup>++</sup>	1 FAAC		
Mg <sup>++</sup>	-109.01	1	0.0	1 Mg <sup>++</sup>			
MgCl <sup>+</sup>	-139.70	3	-2.87	1 Mg <sup>++</sup>	1 Cl <sup>-</sup>		
MgCO <sub>3</sub>	-239.61	1	-11.48	1 Mg <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
MgHCO <sub>3</sub>	-250.74	1	-34.28	1 Mg <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
MgPO <sub>4</sub> <sup>-</sup>	-360.81	2	-15.18	1 Mg <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>		
MgHPO <sub>4</sub>	-375.01	1	-43.17	1 Mg <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>	
MgH <sub>2</sub> PO	-382.46	2	-60.01	1 Mg <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>	
MgOH <sup>+</sup>	-150.08	1	-9.89	1 Mg <sup>++</sup>	1 OH <sup>-</sup>		
MgFAAC	-112.42	E	-9.77	1 Mg <sup>++</sup>	1 FAAC		
Fe <sup>++</sup>	-21.80	1	0.0	1 Fe <sup>++</sup>			
FeCO <sub>3</sub>	-155.21	3	-16.22	1 Fe <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
FeHCO <sub>3</sub>	-165.71	3	-37.97	1 Fe <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
FePO <sub>4</sub> <sup>-</sup>	-277.76	3	-22.21	1 Fe <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>		
FeHPO <sub>4</sub>	-288.74	1	-44.76	1 Fe <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>	
FeH <sub>2</sub> PO	-297.33	1	-63.28	1 Fe <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>	
FeOH <sup>+</sup>	-69.29	1	-14.79	1 Fe <sup>++</sup>	1 OH <sup>-</sup>		
FeOH <sub>2</sub>	-113.29	1	-35.55	1 Fe <sup>++</sup>	2 OH <sup>-</sup>		
FeOH <sub>3</sub> <sup>-</sup>	-148.22	1	-37.99	1 Fe <sup>++</sup>	3 OH <sup>-</sup>		
FeOH <sub>4</sub> <sup>-</sup>	-185.27	1	-39.06	1 Fe <sup>++</sup>	4 OH <sup>-</sup>		
FeFAAC	-27.94	E	-14.38	1 Fe <sup>++</sup>	1 FAAC		
Fe <sup>+++</sup>	-4.02	1	29.96	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>		
FeCl <sup>++</sup>	-37.41	1	22.54	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 Cl <sup>-</sup>	
FeCl <sub>2</sub> <sup>+</sup>	-69.67	1	17.02	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	2 Cl <sup>-</sup>	
FeCO <sub>3</sub> <sup>+</sup>	-147.80	3	-3.76	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup> -1 H <sup>+</sup>
FeHCO	-150.66	3	-12.61	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>
FePO <sub>4</sub>	-265.84	3	-2.15	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 PO <sub>4</sub> <sup>----</sup>	
FeHPO <sub>4</sub>	-280.93	1	-29.42	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>
FeH <sub>2</sub> PO <sub>4</sub>	-283.28	1	-39.61	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>
FeOH <sup>++</sup>	-57.72	1	-0.62	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 OH <sup>-</sup>	
FeOH <sub>2</sub> <sup>+</sup>	-109.63	1	-26.04	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	2 OH <sup>-</sup>	
FeOH <sub>3</sub>	-156.22	1	-51.14	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	3 OH <sup>-</sup>	
FeOH <sub>4</sub>	-201.32	1	-64.63	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	4 OH <sup>-</sup>	
Fe <sub>3</sub> FAA	-23.12	E	-6.30	1 Fe <sup>++</sup>	-1 EL <sup>-</sup>	1 FAAC	
Mn <sup>++</sup>	-55.11	1	0.0	1 Mn <sup>++</sup>			
MnCl <sup>+</sup>	-87.31	1	-5.41	1 Mn <sup>++</sup>	1 Cl <sup>-</sup>		
MnCl <sub>2</sub>	-117.91	1	-8.13	1 Mn <sup>++</sup>	2 Cl <sup>-</sup>		
MnCO <sub>3</sub>	-187.43	3	-14.38	1 Mn <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
MnHCO <sub>3</sub>	-197.84	1	-39.98	1 Mn <sup>++</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
MnOH <sup>+</sup>	-97.35	1	-11.03	1 Mn <sup>++</sup>	1 OH <sup>-</sup>		
MnOH <sub>2</sub>	-138.21	2	-21.39	1 Mn <sup>++</sup>	2 OH <sup>-</sup>		
MnOH <sub>3</sub> <sup>-</sup>	-178.80	1	-29.97	1 Mn <sup>++</sup>	3 OH <sup>-</sup>		
MnPO <sub>4</sub>	-310.11	3	-20.59	1 Mn <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>		
MnHPO <sub>4</sub>	-321.98	3	-44.64	1 Mn <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>	
MnH <sub>2</sub> PO	-328.80	3	-60.17	1 Mn <sup>++</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>	

CHEMICAL COMPOSITION OF ANIMAL MANURE

Appendix A continued.

Species name	$\Delta G_f^\circ$ (kcal mol <sup>-1</sup> )	Ref.	C-param.	Stoichiometry (components)			
MnFAAC	-61.25	E	-14.38	1 Mn <sup>++</sup>	1 FAAC		
Na <sup>+</sup>	-62.59	1	0.0	1 Na <sup>+</sup>			
NaCl	-93.14	E	-2.64	1 Na <sup>+</sup>	1 Cl <sup>-</sup>		
NaCO <sub>3</sub> <sup>-</sup>	-190.50	1	-6.94	1 Na <sup>+</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
NaHCO <sub>3</sub>	-203.20	1	-32.39	1 Na <sup>+</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
NaPO <sub>4</sub>	-310.41	E	-8.47	1 Na <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>		
NaHPO <sub>4</sub>	-326.21	2	-39.15	1 Na <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>	
NaH <sub>2</sub> PO	-334.70	E	-57.50	1 Na <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>	
NaFAAC	-64.32	E	-6.94	1 Na <sup>+</sup>	1 FAAC		
K <sup>+</sup>	-67.51	1	0.0	1 K <sup>+</sup>			
KCl	-98.17	M	-2.81	1 K <sup>+</sup>	1 Cl <sup>-</sup>		
KCO <sub>3</sub> <sup>-</sup>	-194.92	3	-6.09	1 K <sup>+</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
KHCO <sub>3</sub>	-207.61	3	-31.52	1 K <sup>+</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
KPO <sub>4</sub> <sup>-</sup>	-315.28	3	-8.39	1 K <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>		
KHPO <sub>4</sub> <sup>-</sup>	-331.11	3	-39.12	1 K <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>	
KH <sub>2</sub> PO <sub>4</sub>	-339.29	3	-56.95	1 K <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>	
KFAAC	-68.74	E	-6.09	1 K <sup>+</sup>	1 FAAC		
NH <sub>3</sub>	-6.33	1	25.35	1 NH <sub>4</sub> <sup>+</sup>	-1 H <sup>+</sup>		
NH <sub>4</sub> <sup>+</sup>	-18.99	1	0.0	1 NH <sub>4</sub> <sup>+</sup>			
NH <sub>4</sub> Cl	-49.66	E	-2.85	1 NH <sub>4</sub> <sup>+</sup>	1 Cl <sup>-</sup>		
NH <sub>4</sub> CO <sub>3</sub>	-147.08	E	-7.22	1 NH <sub>4</sub> <sup>+</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	-1 H <sup>+</sup>
NH <sub>5</sub> CO <sub>3</sub>	-159.50	M	-32.22	1 NH <sub>4</sub> <sup>+</sup>	1 CO <sub>2</sub>	1 OH <sup>-</sup>	
NH <sub>4</sub> PO <sub>4</sub>	-267.36	E	-9.50	1 NH <sub>4</sub> <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>		
NH <sub>3</sub> PO <sub>4</sub>	-283.13	E	-40.02	1 NH <sub>4</sub> <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>	1 H <sup>+</sup>	
NH <sub>6</sub> PO <sub>4</sub>	-291.28	E	-57.98	1 NH <sub>4</sub> <sup>+</sup>	1 PO <sub>4</sub> <sup>----</sup>	2 H <sup>+</sup>	
NH <sub>4</sub> FAA	-20.89	E	-7.22	1 NH <sub>4</sub> <sup>+</sup>	1 FAAC		

1 = Sadiq & Lindsay, 1979; 2 = Turner et al., 1982; 3 = Sposito & Mattigod, 1980; D = defined; M = measured; E = estimated (see text).



## **Determination of mass balances and ionic balances in animal manure**

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### **Abstract**

Liquid and solid fractions of three different pig slurry samples and a poultry manure sample were isolated through high speed centrifugation followed by ultrafiltration. The gross ionic composition of the liquid manure fractions could be described by:  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ , bicarbonate, weakly acidic cations (ammonium) and weakly alkaline anions (acetate). Ionic balances showed an agreement of more than 98 % between anionic and cationic species. The elemental composition of a pig slurry solid fraction was determined. Mass calculations based on this analysis accounted for 98 % of the total weight.

*Keywords:* alkalinity, analysis, animal manure, cations, liquid fraction, nutrients, volatile fatty acids

### **Introduction**

In recent years the application of large quantities of animal manures<sup>1</sup> to agricultural soils has created environmental problems in the Netherlands. The adverse environmental effects associated with the application of manure include the following:

1. Part of the acidification of forest soils in the Netherlands is considered to be due to atmospheric deposition of ammonia, followed by nitrification. Most of the ammonia stems from manure applied to arable land and grassland (van Breemen et al., 1982).

2. Mobile components such as nitrate and other anions as well as potassium and other univalent cations may leach out to the groundwater. This affects the quality of drinking water sources (Cooper et al., 1984).

3. Phosphate contents in soils, due to the application of large quantities of animal manure, may reach levels of saturation or near-saturation of the phosphate-binding capacity (Gerritse et al., 1982). Surface runoff of phosphate and organic compounds may cause eutrophication of surface water.

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<sup>1</sup> In the following paragraphs the term 'manure' will be used for animal manures as well as for animal slurries.

4. The mobility of metal ions and phosphate in the soil system may be affected by the introduction of organic matter and as a result of changes in the pH and redox potential after manure application (Shaviv & Jury, 1986; Prasad et al., 1984; Field et al., 1985; Amoozegar-Fard et al., 1980).

The long-term purpose of the present study was to quantify the effect of animal manure on the solubility of metal species and phosphate in the soil aqueous phase. Solubility in combination with soil physical conditions determines metal and phosphate mobility and consequently the environmental impact of animal manure application.

An accurate description of the chemical composition of animal manure is a necessary prerequisite for this study. This paper presents the results of chemical analysis of liquid and solid fractions of animal manure.

The liquid fraction of manure is particularly important as it represents the main mobile phase during the initial period of manure/soil interaction, when microbial degradation has not yet started:

— Up to 50 % of manure organic matter is present in the liquid fraction. After application of manure to agricultural soil, this dissolved organic matter (including carboxylic acid anions and phenolic compounds) is responsible for the solubilization of certain metals through complexation; these metals may originate from the manure (e.g. copper) or from the soil (e.g. aluminum, iron). A relation exists between the degree of solubilization of metals and dissolved organic matter content.

— More than 90 % of the ammonium in manure occurs in the liquid fraction. After nitrification the nitrate formed is an important nutrient and potential pollutant. Potassium, sodium and chloride are also predominantly present in the liquid fraction and may cause local salinity problems in the soil.

— Acid/base buffering ions as bicarbonate, ammonium and volatile fatty acid anions constitute up to 75 % of the ionic species found in the manure liquid fraction. Especially when the manure is applied to soils with a limited buffer capacity, the buffering substances from the manure liquid fraction are contributing factors that induce changes in the soil solution pH. Acidifying effects occur upon the loss of gaseous ammonia or upon nitrification. Loss of carbon dioxide to the gaseous phase results in an increasing pH. Rapid aerobic degradation of volatile fatty acids and other organic compounds raises the pH and reduces the buffer capacity of the liquid phase in the soil/manure system. The pH is a crucial factor, which regulates precipitation/solubilization and sorption processes in the soil/manure system. It has a direct effect on acidity-controlled precipitation/dissolution processes (e.g. calcium, magnesium, manganese salts). Indirectly the pH influences the concentration of organic acid anions with complexing properties (e.g. for iron, copper, aluminum) in the soil solution.

Therefore, an accurate description of the chemical composition of manure is a necessary prerequisite for the investigation of manure/soil interactions. The objectives of the present paper are:

- to describe suitable analytical methods for the determination of the chemical composition of manure,
- to develop methods to determine mass balances for manure and ionic balances

for manure liquid fractions,  
— to report results of chemical analysis of a number of animal manure samples.

## Materials and methods

### *Materials*

Two pig slurry samples (PS-1 and PS-2) and one poultry manure sample (PM) were obtained from Dutch farmers. The manures had been stored in storage tanks for several months. After sampling, the manures were analysed within a few weeks. A part of sample PS-1 was stored at 4 °C for 18 months and then analysed. As the composition had changed during storage, this sample was designated as PS-1/18 to distinguish it from the original sample PS-1.

### *Sample pretreatment*

Samples were passed through 4-mm sieves and homogenized. After high-speed centrifugation (2000 g at 20 °C) the supernatant was filtered through 0.45 µm filters under pressure (manual or mechanical). The centrifugation residue of sample PS-1/18 was recovered from the centrifugation tube and was used for solid fraction analysis.

### *Analytical procedures*

Most methods used are standard methods and are only briefly described. The titration procedure for acid/base buffering ionic species in manure filtrates is described in more detail. In the following outline of the analytical methods the term 'sample' means a convenient aliquot of the manure, the manure filtrate or the (wet) manure centrifugation residue, except when stated otherwise.

*Total solids.* Total solids content of the manures and of the solid fractions of manure were determined by overnight drying at 105 °C and weighing.

*pH, redox potential (Eh).* pH and redox potential (Eh) were measured electrochemically in the freshly prepared filtrate.

*Metal ions.* The sample was digested by heating it to 150 °C in a mixture of sulfuric acid and nitric acid (1:3) on a sand bath. Small amounts of nitric acid were added to replace nitric acid lost due to evaporation until the mixture became slightly yellow to colourless. After cooling, dilution and filtration, lanthanum nitrate was added to avoid phosphate interference. Metal concentrations were determined on a flame-AAS or carbon furnace-AAS apparatus.

*Phosphate.* The sample was boiled with dilute sulfuric acid, in the presence of some potassium persulfate. After filtration the colorimetric reagent (an acid solution of

ammonium heptamolybdate and potassium antimonyl tartrate) and ascorbic acid were added. Absorption was measured at 882 nm. This determination gave the total phosphate concentration.

Orthophosphate was determined by the same method as that used for the total phosphate determination except that:

- the mixture was not boiled but kept at room temperature,
- no potassium persulfate was added.

*Carbon dioxide.* Inorganic carbon was determined as carbon dioxide by measuring the volume of gas formed after addition of a strong acid.

*Chloride.* The sample was ashed at 550 °C in the presence of magnesium oxide, to maintain weakly alkaline conditions. The resulting alkaline ash was dissolved in a minimum amount of concentrated nitric acid and then diluted. Chloride was titrated with a standard solution of mercuric nitrate and a diphenylcarbazide solution in ethanol as the indicator.

*Total sulfur.* The alkaline ash of the sample (cf. the chloride determination), was redissolved in nitric acid and the sulfate concentration was determined gravimetrically as barium sulfate.

*Total nitrogen.* Total nitrogen was determined by a simple Kjeldahl technique without the use of nitrate-reducing catalysts, as nitrates were considered absent at the low redox potential of the manure samples.

*Chemical oxygen demand (COD value).* The sample was heated with a known amount of potassium dichromate in dilute sulfuric acid. The amount of dichromate not used up in the oxidation process was determined through titration with ferrous ion.

*Acid/base buffering ionic species.* Manure filtrate (1-2 ml) was diluted with CO<sub>2</sub>-free distilled water to a volume of 200 ml. The solution was transferred to polythene beakers of 275 ml capacity, sealed with parafilm sheet and stored until analysis within 2 hours. The pH was raised to about 9 by rapidly adding 1 M NaOH to the sample solution under limited access of air. Standard 1 M HCl solution was slowly added under moderate stirring until the first (HCO<sub>3</sub><sup>-</sup>) equivalence point was reached at pH = 7.8. This pH was considered the starting point of the titration. Standard HCl solution was then added rapidly to pH = 2.8. The solution was transferred to a 500-ml glass beaker and nitrogen was passed through the solution using a medium size glass frit to remove carbon dioxide (15 min at a rate of 0.2 l min<sup>-1</sup>); the solution was then returned to the polythene vessel and titrated under moderate stirring with the standard 1 M NaOH solution, adding fixed volumes of 0.025 ml and measuring pH after every addition. Neutrality at pH = 7.0 was determined exactly through slow addition of small portions of the NaOH solution near this equivalence point. The addition was then continued up to pH = 11.2 by introducing fixed volumes of

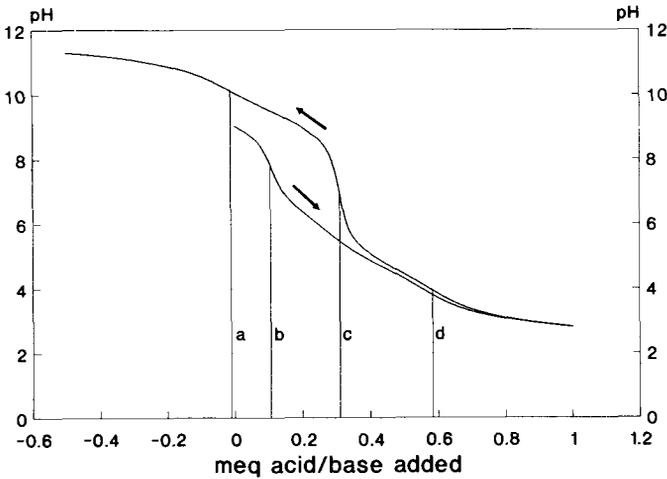


Fig. 1. Titration curve for the determination of acid/base buffering ions in manure filtrate solutions, indicating the equivalence points.

0.025 ml and measuring pH after every addition.

Concentrations were calculated from equivalence points obtained from the titration curves for the onward (HCl) titration and for the backward (NaOH) titration as shown in Fig. 1. The point designated b is the starting point of the titration at pH = 7.8. Point c is the strong acid/base equivalence point at pH = 7.0 and points d and a are the equivalence points for total weak base (mainly volatile fatty acid anions) and total weak acid (mainly ammonium ion), respectively. Points d and a were determined using the excess strong acid/base calculation method, introduced by Gran (1952) and adapted in our laboratory for manure filtrate samples (Japenga, unpublished; Fordham & Schwertmann, 1977).

The concentrations can be calculated as follows:

- weak acid (ammonium ion):  $(c - a)/w$  meq  $g^{-1}$ ,
  - weak base (volatile fatty acid anion):  $d - c/w$  meq  $g^{-1}$ ,
  - bicarbonate:  $(c - b)/w$  meq  $g^{-1}$ ,
- where  $w$  is the sample weight.

*Organic matter.* An aliquot of the centrifugation residue was mixed in a 1:10 ratio with 1M HCl in order to remove carbonates, chloride, ammonium ion and other ionic components. This mixture was centrifuged again and the residue was washed twice with water (1:10) and centrifuged. The final centrifugation residue was dried at 105 °C and weighed. Part of the dry acid-washed centrifugation residue was then ignited at 850 °C; the weight loss upon ignition can be attributed entirely to the oxidative decomposition of organic matter.

*Silica.* The ignition residue (cf. the organic matter determination) was treated several times with concentrated nitric acid and the remaining insoluble matter was weighed

and dried for 4 hours at 180 °C. The residue dissolved (slowly but completely) in hydrofluoric acid, and was thus considered to be silica.

## Results

The gross chemical composition of the manure samples used in this study is summarized in Table 1. For samples PS-1, PS-2 and PM, the concentrations were determined through direct analysis; for sample PS-1/18, most concentrations were calculated from the values obtained separately for the solid and liquid fractions (Tables 2 and 3). The results are in good agreement with average values obtained at routine laboratories in the Netherlands and can be considered to be representative for animal manure, except for phosphorus contents, which were lower than average values.

The chemical composition of the liquid fractions of the manure samples is given in Table 2. The percentages inorganic carbon were calculated from the bicarbonate values.

Table 3 gives the chemical composition of the solid fraction of sample PS-1/18. All elements were determined in the wet centrifugation residue. Results are expressed on a dry weight basis. The wet centrifugation residue amounted to 11.8 % of the original manure. Total solids content of the centrifugation residue (determined through heating overnight at 105 °C) was 26.4 %. The percentages of the different fractions were calculated as follows:

Table 1. Chemical composition of manure samples (concentrations given in g kg<sup>-1</sup>).

	Sample			
	PS-1	PS-2	PM	PS-1/18
Total solids	70	46	183	51.6
COD	53	43	96	26.7
Inorganic carbon	3.5	-	9.5	5.53 (5.47 <sup>a</sup> )
K	6.0	5.3	6.3	5.85 <sup>a</sup>
Na	0.60	0.7	1.3	0.601 <sup>a</sup>
Ca	1.3	0.7	24.0	1.30 <sup>a</sup>
Mg	0.51	0.3	1.8	0.504 <sup>a</sup>
Fe	0.14	0.08	0.33	0.148 <sup>a</sup>
Mn	0.018	0.010	0.061	0.0172 <sup>a</sup>
Cu	0.032	-	0.025	0.032 <sup>a</sup>
Al	-	-	-	0.157 <sup>a</sup>
Cl	2.9	-	3.5	2.73 <sup>a</sup>
P	0.5	-	5.2	0.458 <sup>a</sup>
S	1.4	-	-	1.19 <sup>a</sup>
N-inorganic	-	-	-	5.60 <sup>a</sup>
Silica	-	-	-	1.2 <sup>a</sup>

<sup>a</sup> Calculated from the concentrations obtained for the solid fraction and for the liquid fraction.

- percentage manure centrifugation residue:  $CR = 11.8 \%$
- percentage supernatant:  $C = 100 - CR = 88.2 \%$
- total solids in centrifugation residue:  $SC = 26.4 \%$
- total solids in original manure:  $SM = 5.16 \%$
- total solids in liquid fraction:  $A = (100 \times SM - SC \times CR)/C = 2.32 \%$
- percentage solid fraction:  $S = (SC - A) \times CR / (100 - A) = 2.91 \%$
- percentage liquid fraction:  $L = 100 - S = 97.1 \%$

Therefore the solid fraction of sample PS-1/18 was 2.91 % of the manure, not taking into account volatile material in the solid fraction itself (which presumably is a very small quantity).

11.8 g of the centrifugation residue contained 2.91 g of solid fraction corresponding to 24.7 % solid fraction and 75.3 % liquid fraction. The concentrations of the elements in the solid fraction were calculated from the concentrations determined in the wet centrifugation residue ( $C_{wc}$ ) and in the filtrate ( $C_f$ ) (see Table 2):

$$C_s = (C_{wc} - 0.753 \times C_f) / 0.247$$

Table 2. Chemical composition of the manure liquid fractions (filtrates) (concentrations given in  $\text{g kg}^{-1}$  unless stated otherwise).

	Sample			
	PS-1	PS-2	PM	PS-1/18
COD	-	19.7	32.0	5.39
Inorganic carbon	3.6	2.2	2.6	5.29
K	6.0	5.36	7.35	5.95
Na	0.58	0.74	0.74	0.596
Ca	0.17	0.45	0.30	0.0565
Mg	0.024	0.027	0.034	0.0095
Fe	0.0016	-	0.0057	0.00238
Mn	0.0008	-	0.0007	0.000288
Cu	0.0004	-	0.0003	0.00043
Al	-	-	-	0.00363
Cl	2.9	-	3.2	2.79
P	0.1	-	0.13	0.109
S	0.9	-	-	1.10
N-inorganic	-	-	-	5.42
Weak base (fatty acid anion) ( $\text{eq kg}^{-1}$ )	0.200	0.243	0.137	0.055
Weak acid (ammonium ion) ( $\text{eq kg}^{-1}$ )	0.400	0.277	0.214	0.387
Bicarbonate ( $\text{eq kg}^{-1}$ )	0.304	0.181	0.215	0.441
pH (units)	7.57	7.70	7.47	7.85
Eh (mV)	-400	-420	-375	-480

Table 3. Chemical composition of the solid fraction of sample PS-1/18 (concentrations given in g kg<sup>-1</sup>).

Sample PS-1/18	
COD	736.0
Organic matter	736.0
Inorganic carbon	11.36
K	2.68
Na	0.75
Ca	42.8
Mg	17.0
Fe	4.99
Mn	0.58
Cu	1.09
Al	5.26
Cl	0.7
P	12.09
S	4.06
N-inorganic	11.7
N-organic	28
Silica	41

## Discussion

### *Ionic balance of manure liquid fractions*

The analytical results summarized in Table 2 show that eight different ionic species determine the gross ionic composition of the manure liquid fraction. Major species include Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, weakly alkaline anions (volatile fatty acid anions), weakly acidic cations (ammonium ion) and bicarbonate; Ca<sup>2+</sup> and Mg<sup>2+</sup> occur in smaller amounts. Substantial amounts of phosphorus are present also. About 50 % of total phosphorus in manure filtrates is organically bound. Concentrations of inorganic phosphates (mainly orthophosphate) were estimated to be about 0.005 eq kg<sup>-1</sup> manure liquid fraction as calculated from Table 2. It is not necessary to include phosphates in the ionic balance because they are included in the titrimetrically determined weakly alkaline anions concentration. Sulfur is present in manure filtrates as organic sulfur compounds and as inorganic sulfides, as a consequence of the very low Eh values (< -300 mV). Due to the presence of cations which effectively precipitate inorganic sulfide at the ambient pH, sulphur will be present in the liquid fraction almost exclusively as organic sulfur compounds. This leads to the conclusion that sulfur compounds do not contribute significantly to the ionic balance.

The ionic balance for the liquid fractions of manure samples PS-1, PS-2, PM and PS-1/18 can be calculated as follows.

The equivalent concentrations of the metal ions of interest (Na, K, Ca, Mg, Al) and chloride were calculated from Table 2.

In Table 2 the concentrations of weak base (volatile fatty acid anion), weak acid (ammonium ion) and bicarbonate are expressed as eq kg<sup>-1</sup>. The relative concentration of the different ionic and nonionic species can be computed from their dissociation constants. Results are given for filtrates with pH values ranging between pH = 7.5 and pH = 7.85, taking into account an estimated ionic strength ( $I = 0.55$ ) for the sample; the fatty acid present is considered to be acetic acid:

		pH = 7.5	pH = 7.7	pH = 7.85
'weak base'	free acetic acid	0.06 ‰	0.05 ‰	0.03 ‰
	acetate ion	99.94 ‰	99.95 ‰	99.97 ‰
'weak acid'	ammonia	0.99 ‰	1.56 ‰	2.18 ‰
	ammonium ion	99.01 ‰	98.44 ‰	97.82 ‰
'bicarbonate'	carbonic acid	4.31 ‰	2.72 ‰	1.96 ‰
	bicarbonate	95.24 ‰	96.56 ‰	97.02 ‰
	carbonate	0.45 ‰	0.72 ‰	1.2 ‰

giving the following electrical charges:

	pH = 7.5	pH = 7.7	pH = 7.85
'weak base'	1.000	1.000	1.000
'weak acid'	0.990	0.984	0.978
'bicarbonate'	0.961	0.980	0.991

This means that all electrical charges are close to unity; in reality the electrical charges will be even closer to unity, because of ion pair formation in the manure filtrate at its high ionic strength: especially potassium bicarbonate and ammonium bicarbonate ion pairs increase the bicarbonate and ammonium concentration at the expense of non-charged carbonic acid and ammonia.

For typical manure filtrates estimated net charges, corrected for ion pair formation, are:

	pH = 7.5	pH = 7.7	pH = 7.85
'weak base'	1.00	1.00	1.00
'weak acid'	0.99	0.99	0.98
'bicarbonate'	0.97	0.98	0.99

Corrections for the deviation from unity do not seem necessary for pH values between 7.5 and 7.9 (normal manure values); even if those corrections are carried out, the correction for 'weak acid' (cations) and 'bicarbonate' (anions) are about the same and do not change the ionic balance substantially.

Concentrations in eq kg<sup>-1</sup> for all ionic species with concentrations >0.001 eq kg<sup>-1</sup> are summarized in Table 4. No correction is considered necessary for the deviation from unit electrical charge in the case of the acid/base buffering substances for rea-

Table 4. Equivalent concentrations of ionic species in manure liquid fractions (concentrations in eq kg<sup>-1</sup> liquid fraction).

	Sample			
	PS-1	PS-2	PM	PS-1/18
K	0.153	0.137	0.188	0.152
Na	0.025	0.032	0.032	0.026
Ca	0.009	0.023	0.015	0.002
Mg	0.002	0.003	0.003	0.001
Weak acid (ammonium ion)	0.400	0.277	0.214	0.387
Total (cationic species)	0.589	0.472	0.452	0.568
Cl	0.082	0.051	0.092	0.078
Weak base (fatty acid anion)	0.200	0.243	0.137	0.055
Bicarbonate	0.304	0.181	0.215	0.441
Total (anionic species)	0.586	0.475	0.444	0.574

sons given before.

Differences between the total amount of cations and the total amount of anions do not exceed 2 % in any of the samples.

The results are represented graphically in Fig. 2. Fig. 2a shows the ionic balances for the samples PS-1, PS-2 and PM. Fig. 2b demonstrates the effect of ageing on the ionic balances: sample PS-1 is compared with sample PS-1/18.

From Fig. 2b and from Tables 2 and 4 the following effects of ageing can be observed:

— A decrease in volatile fatty acid anion ('weak base') content accompanied by an equivalent increase in bicarbonate concentration, caused by biological degradation processes.

— Calcium and magnesium levels decreased (as well as manganese levels). This can be attributed to the precipitation of acid-soluble salts such as carbonates and fits with the increase in pH from 7.57 to 7.85. The increase in carbonate-species concentrations (bicarbonate) in the solutions also enhances precipitation. Furthermore, sample PS-1 may have been supersaturated so that slow precipitation occurred during storage.

— Iron and copper concentrations increased slightly. This can be explained by the increase in high molecular dissolved organic matter concentration, associated with the increase of pH. The dependency of metal solubilities on pH and dissolved organic matter content was confirmed by other experiments.

The ionic balance of the sample PS-2 liquid fraction was checked by comparing it with an artificial manure liquid fraction, prepared from the following chemical substances:

- 14.31 g ammonium bicarbonate,
- 1.98 g calcium chloride bihydrate,

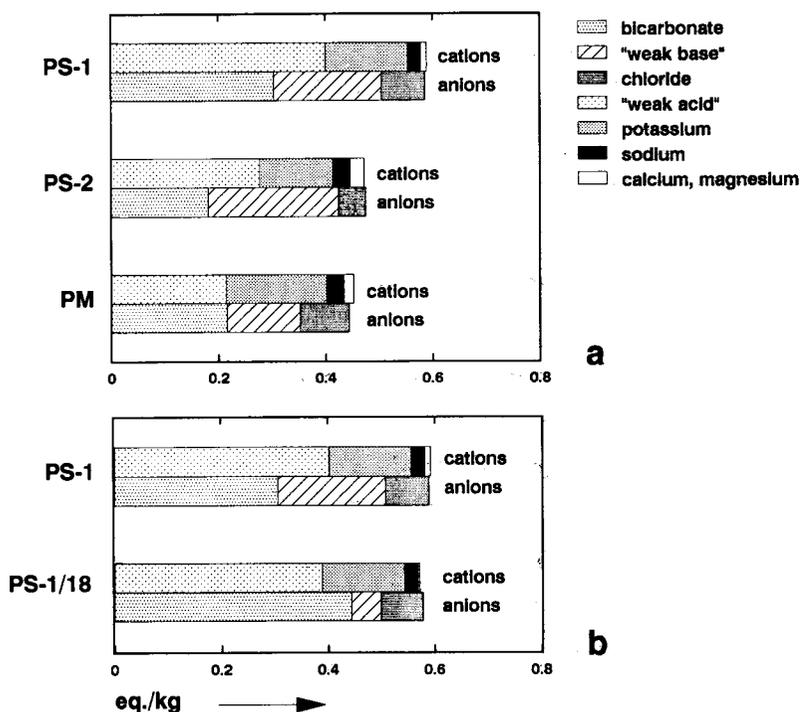


Fig. 2. (a) Ionic balances for manure liquid fractions of PS-1, PS-2 and Pm. (b) Effect of ageing on the ionic balances of pig slurry liquid fraction PS-1.

- 8.82 g acetic acid,
- 1.79 g potassium chloride,
- 7.40 g ammonium acetate,
- 114 ml 1M potassium hydroxide,
- 33 ml 1M sodium hydroxide.

These salts were dissolved in minimal amounts of water, mixed and diluted to 1 litre. This solution approached the chemical composition of the manure liquid fraction from sample PS-2. A small quantity of precipitate was formed (calcium carbonate). Aliquots of this stock solution and of fresh manure filtrate from sample PS-2 were diluted tenfold. The electrical conductivities were compared, showing a value only 0.3 % lower in the case of the prepared solution. This further supports the reliability of the ionic balances determined.

#### Mass balances of sample PS-1/18

From the chemical composition of sample PS-1/18 (Table 1) and of its solid fraction (Table 3), the mass balance could be estimated for the total manure and for the solid fraction.

Table 5. Estimation of the chemical composition of sample PS-1/18 and of the solid fraction of manure sample PS-1/18 (concentrations in g kg<sup>-1</sup>).

	Sample	
	PS-1/18	PS-1/18 (solid fraction)
Organic matter	26.7	736
Carbon dioxide	20.1	41.7
K <sub>2</sub> O	7.0	3.2
Na <sub>2</sub> O	0.8	1.0
CaO	1.8	59.9
MgO	0.8	28.3
FeO	0.2	6.4
MnO	0.0	0.7
CuO	0.0	1.4
Al <sub>2</sub> O <sub>3</sub>	0.3	9.9
Cl	2.7	0.7
P <sub>2</sub> O <sub>5</sub>	1.0	27.7
S	1.2	4.1
NH <sub>3</sub>	6.8	14.2
Silica	1.2	41
Total calculated	70.6	976
Total determined	74.5	1000
Mass accounted for	95 %	98 %

Table 5 represents the composition of sample PS-1/18 and of the sample PS-1/18 solid fraction. Values from Table 1 and 3 were used with the following modifications:

- metal species are represented as oxides,
- inorganic nitrogen is represented as ammonia,
- sulfur is represented as sulfide,
- phosphorus is represented as phosphorus pentoxide,
- inorganic carbon is represented as carbon dioxide.

These species will be the approximate 'building stones' of the compounds present in sample PS-1/18 and in the sample PS-1/18 solid fraction; only an additional unknown amount of hydrogen is present in the components. The total solids content of sample PS-1/18 was computed from data in Table 5 (first column) and equals 70.6 g kg<sup>-1</sup>. The experimentally determined total solids content is 51.6 g kg<sup>-1</sup>. Considering, however, that ammonium ion is predominantly present in the liquid phase and that at pH values of 7-8 inorganic carbon in the liquid phase is present as bicarbonate, it may be expected that during drying at 105 °C a major part of the ammonium bicarbonate decomposed and evaporated as ammonia and carbon dioxide; together with 6.4 g kg<sup>-1</sup> ammonia from the liquid fraction, 16.5 g kg<sup>-1</sup> of car-

bon dioxide can evaporate. This gives a corrected experimental total solids content of  $51.6 + 6.4 + 16.5 = 74.5 \text{ g kg}^{-1}$  in the case of total evaporation of ammonium bicarbonate from the liquid fraction; this agrees reasonably well with the calculated value ( $70.6 \text{ g kg}^{-1}$ ).

From the calculated and corrected experimentally determined values a mass balance coefficient can be calculated:

(1)  $\text{MB (sample PS-1/18)} = 70.6/74.5 = 0.95$

The missing 5 % can be ascribed, at least partially, to hydrogen in the dry matter present in salts as hydrogenophosphates, as crystal water or as strongly adsorbed water.

For the solid fraction of manure sample PS-1/18, Table 5 shows a calculated total solids content of  $976 \text{ g kg}^{-1}$ . The mass balance coefficient can be calculated now:

(2)  $\text{MB (sample PS-1/18 solid fraction)} = 976/1000 = 0.98$

The missing 2 % can be accounted for by the presence of hydrogen in the dry material. Analytical inaccuracies (especially in the relationship between organic carbon and organic matter content and in the DOC measurement itself) may be of some importance too.

In Fig. 3 the mass balances are presented; the sum of the experimentally determined total solids content and the amount of ammonium bicarbonate considered to be evaporated during drying is taken as 100 % in the case of sample PS-1/18.

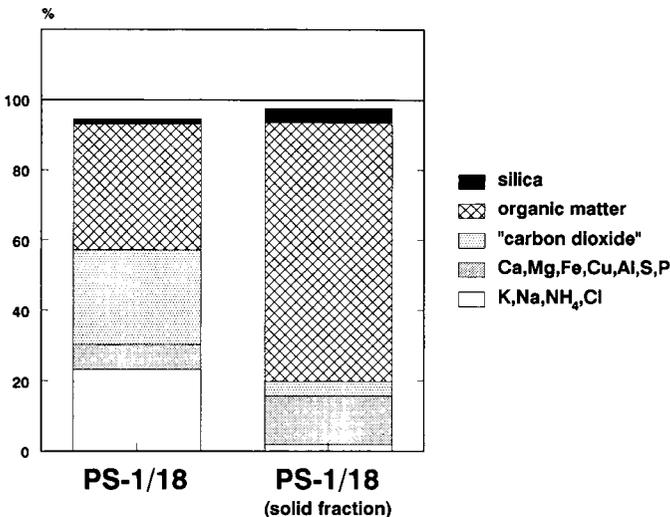


Fig. 3. Calculated mass for sample PS-1/18 and for the solid fraction of sample PS-1/18.

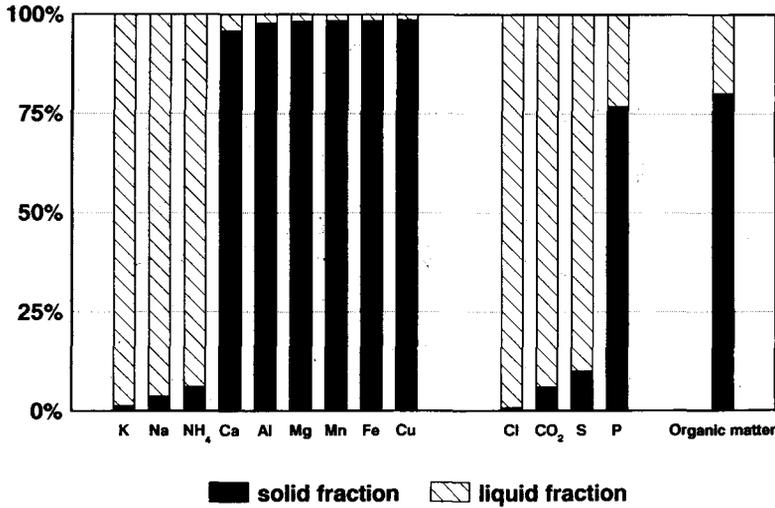


Fig. 4. Distribution of components over the solid and liquid fractions of sample PS-1/18.

*Distribution ratios*

The distribution of main manure components between the two fractions was calculated based on concentrations in the two fractions and the relative amounts of the fractions (liquid fraction 97.1 %; solid fraction 2.91 %). The results are given in Fig. 4.

Distribution ratios can be calculated too:

$$k = C_s / C_l$$

in which:

$C_s$  = concentration in the solid fraction,

$C_l$  = concentration in the liquid fraction.

Values for  $C_s$  and  $C_l$  are obtained from Tables 3 and 2, respectively, and the resulting values for the distribution ratio  $k$  are summarized in Table 6.

**Conclusion**

The results given for the mass balances and ionic balances in the manure chemical system show that with a limited number of chemical analyses (using standard procedures) a good description of the manure chemical system can be given. Reliable data sets obtained in this way can be used for the development and subsequent testing of a chemodynamical model of the soil/manure system.

Ionic balances for manure solid fractions can be determined as soon as reliable analytical methods will be available for distinguishing between inorganically and organically bound sulfur and phosphorus.

MASS AND IONIC BALANCES IN ANIMAL MANURE

Table 6. Distribution ratios between the solid and liquid fractions of sample PS-1/18 ( $k = C_s/C_l$ ).

Sample PS-1/18	
Organic carbon	135
Inorganic carbon	2.1
K	0.5
Na	1.3
Ca	750
Mg	1800
Fe	2100
Mn	2000
Cu	2550
Al	1450
Cl	0.3
P	110
S	3.7
N-inorganic	2.2

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## **Contribution of atmospheric deposition to heavy-metal concentrations in field crops**

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### **Abstract**

The contribution of atmospheric deposition to the concentrations of Cd and Pb in four crops was studied by growing plants under field conditions, and, as a reference, in a dust-free chamber on soil labelled with Cd-109 or with Pb-210. The contribution of soil-borne Cd and Pb was distinguished from that of the deposition by measuring the isotope dilution in the plant. The 'specific activity' of the plant material grown in the field was compared with that in the dust-free environment. Atmospheric deposition contributed considerably (73-95 %) to the Pb concentrations in the leafy material of grass, spinach and carrot, and of wheat grain and straw. The contribution of deposition to the Cd concentrations of these crops was significant only in wheat grain and straw.

*Keywords:* atmospheric deposition, cadmium, lead, heavy metals, carrot, grass, spinach, wheat

### **Introduction**

In most industrialized countries the heavy-metal contents of soils tend to increase gradually (Smilde, 1989; Tjell et al., 1979). This is the result of surpluses in the balance of inputs to the topsoil from deposition, fertilizers and waste products, and the output from leachates to the subsoil, and from harvested products. Atmospheric pollution, in the form of metal-containing aerosols, is a significant factor in this imbalance. If soil properties remain unchanged, the gradual increase in soil metal levels will result in a corresponding increase in plant metal concentrations. These effects can be detected only after relatively long periods of time.

Plants are also exposed directly to metal-containing aerosols and precipitation (ter Haar, 1970; Lagerwerff, 1971; Rabinowitz, 1972; Tjell et al., 1979; Harrison, 1989). Part of the metals precipitating on the plant surface is taken up, and is involved in plant metabolism (Dollard, 1986). The contribution to plant metal levels may be considerable and may exceed that of the soil (Tjell et al., 1979; Hovmand et al., 1983; Harrison & Chirgawi, 1985; Harrison & Johnston, 1987).

An elegant technique to identify the origin of plant metal is to label the soil with a radioactive metal. Radioactivity found in the plant is specific for soil-borne metal.

In this study, radioactive cadmium (Cd) and lead (Pb) were used on plants grown at a field location and in a dust-free environment.

### Materials and methods

#### *Determination of the contribution of airborne metals to metal concentrations in field crops*

The contribution of the soil to heavy-metal concentrations in plants can be distinguished from that of the atmospheric deposition by growing plants on labelled soil and determining the isotope dilution in the plants. The added nuclide is equilibrated with the indigenous soil metal, by intensive mixing of the soil with a metal solution, and keeping it at least six months under moist conditions (Tjell et al., 1979; Hovmand et al., 1983; Harrison & Chirgawi, 1985, Harrison & Johnston, 1987). Specific activities of the metal are measured in soil and in plant material. The specific activity is defined as the radioactivity per unit weight of metal, expressed in becquerel per mg metal ( $\text{Bq mg}^{-1}$ ).

The metal concentration  $c_p$  in the plant is the sum of the metal concentrations  $c_a$  and  $c_s$  derived from uptakes from the atmosphere and the soil, respectively:

$$c_p = c_a + c_s \quad (1)$$

Dividing both sides of Equation 1 by  $c_p$  shows that the fractions  $c_a/c_p$  and  $c_s/c_p$  of metal derived from the atmosphere and the soil are related by

$$c_a/c_p = 1 - c_s/c_p \quad (2)$$

To determine the ratio  $c_s/c_p$ , the soil is labelled with a radioactive isotope of the metal. Let  $x_p$  be the specific activity of the metal in the plant, and let  $x_a$  and  $x_s$  be the specific activities of the metal derived by the plant from the atmosphere and the soil, respectively. Then the radioactive metal concentration  $x_p c_p$  in the plant is given by:

$$x_p c_p = x_a c_a + x_s c_s \quad (3)$$

Let  $x_0$  be the background specific activity of the metal. Then multiplying Equation 1 by  $x_0$ , subtracting the result from Equation 3, assuming that  $x_a = x_0$ , and rearranging gives:

$$c_s/c_p = (x_p - x_0)/(x_s - x_0) \quad (4)$$

Introducing Equation 4 into Equation 2 gives:

$$c_a/c_p = 1 - (x_p - x_0)/(x_s - x_0) \quad (5)$$

Equation 5 has been used regularly in studies of uptake of metals (Tjell et al., 1979; Hovmand et al., 1983; Harrison & Chirgawi, 1985, 1988). Determining the specific activity ( $x_s - x_0$ ) of the metal taken up by the plant from the soil on the basis of soil chemical analysis turned out to be rather difficult.

Growing plants on the same labelled soil in a dust-free environment provides an alternative direct means of determining the specific activity. Let a superscript \* denote quantities associated with uptake in such a dust-free environment. Then, analogous to Equations 1 and 4:

$$c_p^* = c_s^* \quad (6)$$

$$c_s^*/c_p^* = (x_p^* - x_0)/(x_s^* - x_0) \quad (7)$$

Substituting Equation 6 in Equation 7 and assuming that the specific activity ( $x_s^* - x_0$ ) of the metal taken up from the soil in the dust-free environment is equal to the specific activity ( $x_s - x_0$ ) of the metal taken up from the same soil in the outdoor environment, then Equation 7 reduces to:

$$(x_s - x_0) = (x_p^* - x_0) \quad (8)$$

Introducing Equation 8 into Equation 5 gives:

$$c_a/c_p = 1 - (x_p - x_0)/(x_p^* - x_0) \quad (9)$$

According to Equation 9 the relative contribution  $c_a/c_p$  of airborne metal can be calculated on the basis of measurements of specific activities ( $x_p - x_0$ ) and ( $x_p^* - x_0$ ) of plants grown on the same labelled soil in the outdoor and dust-free environments, respectively. Based on these considerations experiments were performed to determine the contribution of airborne metals to metal concentrations in field crops.

### Soils

Two sandy loam soils were selected, low in Cd and Pb and with a neutral reaction. The main properties are given in Table 1. The soils were passed through a 2-mm titanium sieve before subsampling. Carrier-free Cd-109 and Pb-210 were, dissolved

Table 1. Properties of the two sandy loam soils.

	General characteristics						Cadmium		Lead	
	pH	org.mat.	CaCO <sub>3</sub>	<2 $\mu$ m	<16 $\mu$ m	<50 $\mu$ m	mg kg <sup>-1</sup>	MBq mg <sup>-1</sup>	mg kg <sup>-1</sup>	MBq mg <sup>-1</sup>
Soil 1	7.8	0.88 %	2.1 %	3.5 %	4.2 %	14.4 %	0.16	2.4	4.7	313.0
Soil 2	6.8	1.74 %	0.1 %	6.4 %	12.3 %	22.9 %	0.29	2.0	20.1	143.6

in a slightly acidified solution, added to a slurry of the soil, and thoroughly mixed in an epoxy-coated cement mixer. After drying to field capacity the soils were equilibrated under moist conditions for six months. The labelled soils were placed on top of a gravel layer in polyethylene containers. The soil surfaces (8.6 dm<sup>2</sup>) of the pots were covered with a layer of polyethylene granules. This prevented contamination of the plants due to splashing of soil particles during rain. Excess rainwater was removed via a tube positioned in the gravel layer at the bottom of the container.

### *Plants*

Plant species were selected differing in leaf surface and in edible organs (leaves, seeds, tubers): grass (*Lolium multiflorum* Lam., Italian ryegrass), spinach (*Spinacia oleracea* L. cv. Mazurka), spring wheat (*Triticum aestivum* L. cv. Adonis) and carrots (*Daucus carota* L. cv. Cornet RZ). Grass was grown on soil 1 in 1984 and 1985. Spinach, carrots and spring wheat were grown on soil 2 in 1986 and 1987.

### *Cultivation*

Each experiment consisted of two sets of six containers: two untreated soils, two soils labelled with Cd-109, and two soils labelled with Pb-210. One set of containers was placed outside in a lawn with the rims level with the surrounding grass plot. The containers were exposed to wet and dry deposition. The second set was placed in a dust-free growth chamber (DGC) in a greenhouse.

Fertilization, watering, and pest control were performed according to the standards for the relevant crops. Metal contamination was avoided by using high purity reagents and metal-free equipment.

The dust-free growth chamber is similar to open-top chambers used in air pollution studies (Buckenham et al., 1981). Ambient air was supplied through a pre-filter/HEPA filter system that excluded 99.999 % of particles > 0.3 μm. The growth chamber (floor surface 4.4. m<sup>2</sup>) was made of perspex. The 'top' of the chamber was covered with a perspex lid; air could escape from the room through a 7-cm slit between cover and walls. The levels of Cd and Pb in the air of the DGC were low, but not negligible: 0.02 ng m<sup>-3</sup> and 0.29 ng m<sup>-3</sup>, respectively. This was probably caused by some leakage of unfiltered air through the service door and through the exit slit. Also some transport of extremely small metal-containing particles through the HEPA-filter might have occurred (Lee et al., 1968).

### *Sampling procedure and sample treatment*

Utmost care was taken to avoid sample contamination during handling of the samples. Grass was harvested fortnightly, spinach, spring wheat and carrots once, at maturity. Plant material was oven-dried and ground; it was not rinsed because it was found that the results were not affected by rinsing the leaf material with distilled water. Carrot roots were freed from soil particles and rinsed with a detergent solution (T-pol).

*Sampling of air and bulk atmospheric deposition*

Bulk deposition was collected throughout the experimental periods for determination of Cd and Pb, using standardized open precipitation collectors, as used at the time by the National Precipitation Network (RIVM, 1984-1987). Particulate Cd and Pb in air were collected with a dust-collection apparatus (Sartorius), fitted with a membrane filter with a maximum pore diameter of 0.3  $\mu\text{m}$ .

*Analytical methods**Macroconstituents in soils*

Macroconstituents (particle size distribution, organic matter, calcium carbonate, pH in 1M KCL-extract) were determined by standard analytical methods.

*Total and extractable Cd and Pb contents of soils*

Total Cd and Pb were obtained by digesting the soil five times with concentrated  $\text{HNO}_3$  (Balraadsing, 1974). Four soil extractants (Andersson, 1975) were used, namely:

- 1 M  $\text{NH}_4$ -acetate, pH 7.0,
- 1 M  $\text{NH}_4$ -acetate, pH 4.8,
- 0.025 M EDTA, pH 7.0,
- 2 M  $\text{HNO}_3$ .

The dry soil sample (15 g) was shaken for 1 h with 50 ml of the extractant, and separated from the liquid fraction by centrifugation and filtration. Cd and Pb were determined by flameless atomic absorption spectrometry, after solvent-extraction at pH 3.5 by methyl isobutyl ketone (MIBK) with a mixture of 1 % ammonium pyridindithiocarbamate (APDC) and sodium diethyldithiocarbamate (DDC) solution in ethanol as a complex former and subsequently back-extraction by 2 M  $\text{HNO}_3$ . The EDTA-extract was digested with  $\text{HNO}_3$  before liquid-liquid extraction. Standard additions were made if required.

*Total Cd and Pb contents of plants*

Plant material was digested by boiling it with concentrated  $\text{HNO}_3$ . After addition of diluted HCl and refluxing during one hour at 100 °C the digest was filtered. Cd and Pb were determined by flameless atomic absorption spectrometry, after liquid-liquid extraction as described.

*Radioactivity in soils and plants*

Pb-210 and Cd-109 activities were counted by gamma-spectrometry in the solutions obtained by digestion or extraction of soils and plants. When activities were low, a higher count rate was obtained for the Pb-210 activity by using the 1.14 MeV beta from Bi-210, the daughter activity from Pb-210 (Karamanos et al., 1975). Bi-210 grows in completely after 50 days and its Cerenkov light can be counted in a liquid scintillation counter.

**Results**

*Distribution of labelled Cd and Pb over soil fractions*

The distribution of total and radioactive Cd and Pb over the soil fractions was determined by extracting the labelled and equilibrated soils with various extractants, differing in strength. If the labelled metals would be uniformly distributed over the binding forms of the soil, the specific activities of the metals in all fractions would be the same. The results of the experiments (soils 1 and 2 combined) show that the specific activities of the metals decreased when a larger proportion of the soil metal was extracted (Fig. 1). Therefore, Equation 5 cannot be used to calculate the contribution of the atmospheric deposition to plant metal concentrations.

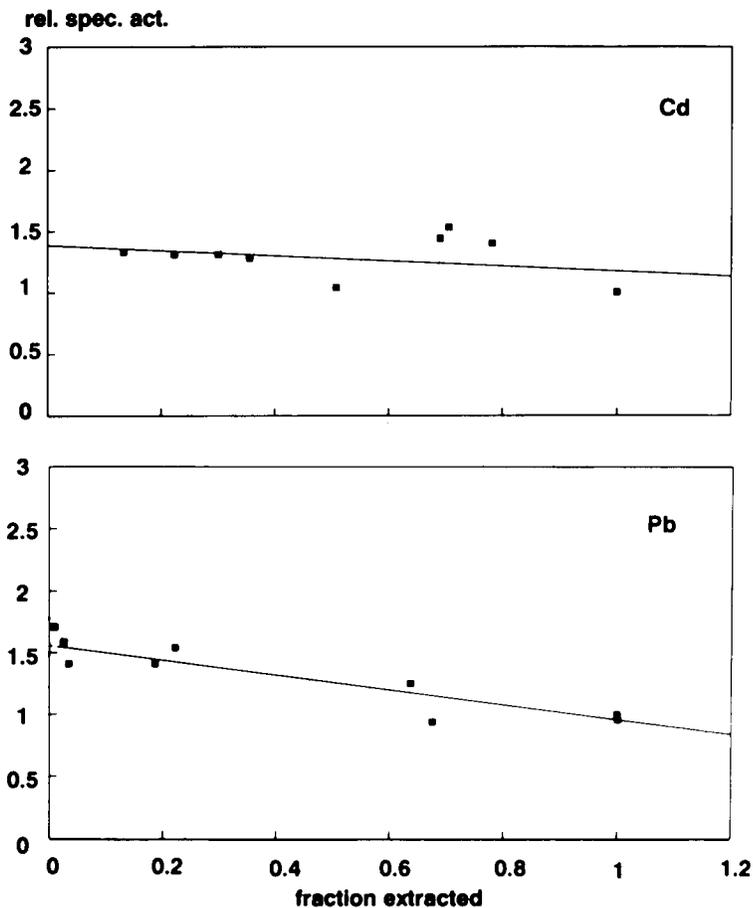


Fig. 1. Relative specific activity of Cd-109 (top) and Pb-210 (bottom) in soil extracts. (Relative specific activity of total soil Cd or Pb = 1.)

*Contribution of airborne metal to plant metal concentrations*

The quantities of Cd and Pb supplied to the experimental plot were collected in open bulk-deposition collectors and measured. The results were compared with the average quantities in the Netherlands (Table 2). In the last experimental year (1987), both Cd and Pb deposition levels at the experimental plot were higher than the average levels in the country, possibly because of building activities in the neighbourhood. The annual supply of Cd to the soil was of the same order of magnitude as the net annual removal by agronomic crops on arable land, estimated to be 1.4 g ha<sup>-1</sup> (Smilde, 1989). The supply of Pb to the soil was much higher than the removal of 1.5 g Pb ha<sup>-1</sup> by crops. The airborne Cd supplied during the growing period was lower in all investigated crops than the Cd content of these crops. This is in contrast to Pb, where the airborne Pb supply exceeded the contents of the crops. The quantities of Cd and Pb that were actually intercepted by the experimental plants were estimated by means of the isotope dilution technique.

*Cd experiments*

The results of the plant experiments in the field and under dust-free growing conditions are summarized in Table 3.

The (total) Cd concentrations of the plants grown in the dust-free chamber were equal to (spring wheat) or higher than (other species) those of the field-grown plants, whereas the dry-matter yields in the DGC were equal (spring wheat) or lower (other species). The higher plant Cd concentrations in the DGC might be due to a reversed dilution effect, and environmental conditions could also be involved. Soil type, treatment, planting/sowing time and period of cultivation were exactly the same, but in the DGC both air and soil temperature were higher than those under field conditions. The higher wind velocity in the DGC led to a higher rate of plant transpiration, which may have caused a greater convective transport to the soil/root interface. The higher plant Cd concentrations illustrate the strong impact of growing conditions on Cd uptake.

Table 2. Cd and Pb in wet deposition and in air.

	Cd and Pb in wet deposition (g ha <sup>-1</sup> yr <sup>-1</sup> )				Cd and Pb in air (ng m <sup>-3</sup> )					
	Netherlands <sup>1</sup>		Haren		Netherlands <sup>1</sup>		Haren		DGC <sup>2</sup>	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
1984	1.9	128	1.7	74	2	177	1.0	107	0.09	0.63
1985	2.0	122	1.9	82	-	168	4.0	26	0.02	1.27
1986	1.5	93	1.6	50	7	126	0.3	32	0.003	0.00
1987	1.6	85	2.1	127	7	100	0.5	25	0.00	0.02

<sup>1</sup> Average in the Netherlands (RIVM, 1984-1987).

<sup>2</sup> DGC = dust-free growth chamber (incidental measurements).

Table 3. Concentrations and specific activities of Cd in soil and in plants, grown in the field and in a dust-free growth chamber (DGC).

	Field conditions				Dust-free conditions			
	yield <sup>1</sup> (kg m <sup>-2</sup> )	conc. (mg kg <sup>-1</sup> )	spec. act. (MBq mg <sup>-1</sup> )	SD <sup>2</sup> (MBq mg <sup>-1</sup> )	yield <sup>1</sup> (kg m <sup>-2</sup> )	conc. (mg kg <sup>-1</sup> )	spec. act. (MBq mg <sup>-1</sup> )	SD <sup>2</sup> (MBq mg <sup>-1</sup> )
Soil 1		0.158	2.44	0.48		0.158	2.44	0.48
Grass 1984	3.35	0.170	3.47	0.05	1.86	0.406	3.74	0.05
Grass 1985	1.78	0.162	3.42	0.05	1.57	0.226	3.32	0.05
Soil 2		0.287	1.98	0.05		0.287	1.98	0.05
Spinach 1986	0.37	1.150	3.27	0.18	0.22	1.48	3.18	0.23
Carrot roots 1986	2.52	0.206	2.60	0.22	2.14	0.238	2.29	0.31
Carrot leaves 1986	0.95	0.344	2.52	0.11	0.85	0.428	2.48	0.16
Wheat grain 1987	1.62	0.106	1.91	0.16	1.78	0.089	2.43	0.20
Wheat straw 1987	1.60	1.163	1.21	0.08	1.72	0.094	2.34	0.11

<sup>1</sup> On dry-matter basis.<sup>2</sup> Standard deviation.

Comparison of the specific activities (Table 3) of plant Cd shows that for grass, carrots and spinach no significant contribution of airborne Cd could be demonstrated (Table 4). This contribution was negative and resulted from higher specific activities observed in some field plants as compared with the dust-free plants. The supply of Cd via atmospheric deposition was small compared with the amount taken up from the soil. There was a significant contribution only in spring wheat, both for straw and grain. This means that not only metal aerosols adhering to the leaf surface

Table 4. Soil- and air-borne Cd and Pb in crops.

	Cd					Pb				
	n <sup>1</sup>	soil- borne (µg m <sup>-2</sup> )	air- borne (µg m <sup>-2</sup> )	SD <sup>2</sup> (µg m <sup>-2</sup> )	air- borne (%)	n <sup>1</sup>	soil- borne (µg m <sup>-2</sup> )	air- borne (µg m <sup>-2</sup> )	SD <sup>2</sup> (µg m <sup>-2</sup> )	air- borne (%)
Grass 1984	66	282	22	6	7.3	66	124	2521	3	95
Grass 1985	36	155	-5	4	-2.9	36	144	1532	2	91
Spinach 1986	12	209	-6	20	-2.8	6	77	212	29	73
Carrot roots 1986	8	249	-33	45	-13.2	8	127	8	19	5.7
Carrot leaves 1986	12	168	-3	14	-1.7	12	32	1254	7	98
Wheat grain 1987	4	64	18	8	21.4	4	0	337	53	100
Wheat straw 1987	4	67	63	5	48.4	4	3	1032	2	99.7

<sup>1</sup> Number of observations.<sup>2</sup> Standard deviation.

contributed to plant Cd but also metal absorbed by the leaves and translocated to the seed. The spring wheat experiments demonstrate that a much longer exposure to atmospheric deposition can lead to a significant contribution of aerosol Cd to plant Cd.

### *Pb experiments*

The results are summarized in Table 5. The (total) Pb content of the plant material grown in the field was markedly higher than that of the plants grown under dust-free conditions. In the case of Cd, the differences in growing conditions caused higher Cd concentrations in plants in dust-free conditions; in the case of Pb they were masked by the strong effects of airborne Pb and by the low uptake of soil Pb. The differences in specific activities of Pb in plants grown under field conditions and in the chamber demonstrate the dominant effect of airborne Pb. The contribution of airborne Pb, calculated with Equation 9, amounts to over 90 % for grass, carrot leaves, and wheat grain and straw (Table 4). Lower contributions were calculated for spinach (73 %), and carrot roots (5.7 %) (Table 4). The lower contribution for spinach can be attributed to the short growing period, those for carrot roots to the indirect supply of airborne Pb to the organs. Table 5 also shows that in most plants grown under dust-free conditions the specific activities were equal or lower than those of total soil-Pb. This suggests that the residual Pb contamination of the air of the DGC had a significant effect on plant Pb concentrations, leading to a small underestimation of the contribution of airborne Pb.

Table 5. Concentrations and specific activities of Pb in soil and in plants grown in the field and in a dust-free growth chamber (DGC).

	Field conditions				Dust-free conditions			
	yield <sup>1</sup> (kg m <sup>-2</sup> )	conc. (mg kg <sup>-1</sup> )	spec. act. (KBq mg <sup>-1</sup> )	SD <sup>2</sup> (KBq mg <sup>-1</sup> )	yield <sup>1</sup> (kg m <sup>-2</sup> )	conc. (mg kg <sup>-1</sup> )	spec. act. (KBq mg <sup>-1</sup> )	SD <sup>2</sup> (KBq mg <sup>-1</sup> )
Soil 1		4.69	313.02	89.91		4.69	313.02	89.91
Grass 1984	3.78	1.48	1.48	0.01	2.28	0.120	31.38	0.22
Grass 1985	2.07	1.73	1.30	0.01	1.90	0.093	15.13	0.11
Soil 2		20.10	143.56	5.74		20.1	143.56	5.74
Spinach 1986	0.33	1.59	3.48	0.62	0.13	0.12	13.10	4.26
Carrot roots 1986	2.35	0.11	134.31	9.40	2.33	0.115	142.45	19.37
Carrot leaves 1986	1.13	2.60	3.00	0.49	1.13	0.135	119.88	10.91
Wheat grain 1987	1.51	0.43	d.l. <sup>3</sup>	-	2.08	0.013	d.l. <sup>3</sup>	-
Wheat straw 1987	1.62	1.30	0.15	0.02	1.85	0.037	44.40	29.30

<sup>1</sup> On dry-matter basis.

<sup>2</sup> SD = standard deviation.

<sup>3</sup> d.l. = below detection limit.

## Discussion

Various techniques have been used to estimate the contribution of soil and atmosphere to the metal content in field crops. Tjell et al. (1979), Hovmand et al. (1983) and Harrison & Johnston (1987) used the radioactive tracer technique mentioned before, based on Equation 5. Our study demonstrates that the relationship between the specific activities of soil and plant cannot always be used to estimate the content of soil-borne metals in plants. Harrison & Johnston (1987) used two other techniques to determine the relative contributions of atmosphere and soils to the Pb content of crops:

— The dual-compartment chamber technique, in which plants are cultivated in filtered air or in unfiltered, ambient air. This technique provides specific information on the contribution of dry deposition.

— A technique in which plants are grown in a common soil at field sites differing in atmospheric Pb deposition levels. The local atmospheric deposition is monitored with moss-bag collectors. Soilborne Pb is estimated by extrapolation of plant Pb levels to zero deposition.

The moss-bag collector probably better monitors plant-related Pb deposition than bulk deposition, but the differences between plant species in intercepting atmospheric Pb are not accounted for. Moreover, because of inevitable differences in growing conditions an error is introduced leading to a large bias in the conclusions. The authors conclude that the contribution of particulate Pb in air (dry deposition) is much larger than that of wet deposition.

The technique used in our study, in which specific activities of plants grown in the field and under dust-free conditions are compared, does not require estimation of a plant-available fraction in soil, and is not sensitive to differences in environmental growing conditions.

The results show a significant contribution of atmospheric deposition to crop Pb concentrations, and, for spring wheat, also to crop Cd concentrations. For Pb, these conclusions agree with the results of other studies (Tjell et al., 1979; Hovmand et al., 1983). For a proper comparison, soil conditions (metal levels and availability) as well as deposition rates have to be considered. Hovmand et al. (1983) and Tjell et al. (1979) used sandy loam and sandy soils with a moderate pH ( $\text{CaCl}_2$ ) of 6.3 and 4.6, and relatively low Cd (0.08 and 0.09 mg kg<sup>-1</sup>) and Pb (14.4 and 11.1 mg kg<sup>-1</sup>) levels, combined with relatively low Cd and Pb deposition levels. Under these conditions the contributions of soilborne Cd and Pb are low, and the relative effect of airborne metals is high. In our experiments, soil Cd and Pb levels and pH were higher and the deposition is of the same order of magnitude, also leading to low Cd and Pb levels in the plants. In our studies, corresponding Cd levels were found for wheat grain and straw, but no significant contribution of airborne Cd could be detected in grass and carrot roots and leaves as were found by Hovmand et al. (1983), who observed contributions of airborne Cd of up to 52 %

The results of Harrison et al. (1987) on Pb cannot be compared with our results, as no information is given on the bulk deposition rate.

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# **Heavy metals and organic micropollutants in floodplains of the river Waal, a distributary of the river Rhine, 1958-1981**

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## **Abstract**

During periods of high water discharge, dyke-protected floodplains of the river Rhine in the Netherlands become inundated and suspended matter from the river settles out. In the last 30 years, floodplain top layers have been sampled several times just after deposition; samples were dried and stored in a specimen bank. We used these samples to assess the development of sediment contamination with heavy metals and organic micropollutants during the past decades. Heavy metals investigated include zinc, copper, chromium, lead, cadmium, nickel, mercury and arsenic. Different groups of chemically persistent organic micropollutants were studied: polycyclic aromatic hydrocarbons (PAH); polychlorobiphenyls (PCB), hexachlorobenzene (HCB), DDT and DDT-metabolites. In general, the levels of most contaminants decreased substantially between 1958 and 1981. The variation among the different floodplain locations is due to differences in hydrodynamic characteristics of the location. A comparison was made between the concentrations found and the levels considered acceptable if the floodplain area is used for cattle grazing; a comparison was made also with estimated natural background levels and with reference values defined by the Dutch government.

*Keywords:* cadmium, floodplains, heavy metals, mercury, organic micropollutants, PCB's, Rhine

## **Introduction**

During spring, water discharges in the river Rhine increase, causing inundation of the floodplains along the river and along its branches in the Netherlands. During the inundation periods, suspended solids settle on the floodplain, leaving behind a thin layer of sediment (about 1-5 mm).

Figure 1 shows a cross section of a typical floodplain/river system in the lower Rhine area. Generally, a low summer dyke and a high winter dyke are part of the system (right-hand side of Fig. 1). At some locations, however, no summer dyke is present (left-hand side of Fig. 1). The summer dyke protects the area between the two dykes during periods of normal and moderately increased water discharges, making cattle grazing and brick production possible during the summer period.

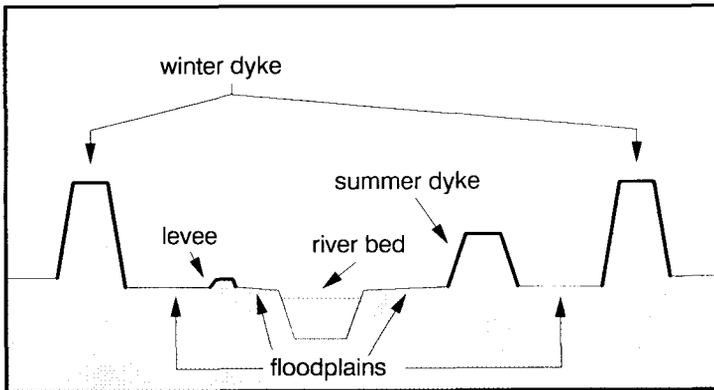


Fig. 1. Cross section of a typical dyke-protected floodplain system in the Dutch lowland.

With increasing water discharge the area within the summer dykes becomes inundated first and finally the area between the summer and winter dykes; this last event takes place only at high water discharge, on average once every two years. The entire land area between the winter dykes is generally considered as floodplain. The total floodplain area along the river Rhine and its distributaries in the Netherlands is about 40 000 ha.

Freshly deposited sediment from the floodplain areas has been sampled for different purposes since 1958. Sampling took place through the careful removal of freshly deposited material immediately after the floodplain area fell dry; the samples were taken by the same technician from 1958 to 1981, which reduced variation in sampling technique to a minimum. The fact that the samples were stored in a specimen bank gave an excellent opportunity to investigate the changes in floodplain contamination during the last decades.

Contaminant levels in the floodplain sediments are important:

- as an indication of river pollution,
- in relation to plant uptake (generally grass), and
- in relation to animal uptake through the consumption of polluted grass but also through direct ingestion of soil.

## Materials and methods

### *Sampling scheme*

Figure 2 shows all sampling locations involved in this study: sampling areas situated between summer and winter dykes and sampling areas not separated from the river bed by a summer dyke are indicated.

Heavy-metal concentrations were determined in samples from 13 different locations along the river Waal, the largest distributary of the river Rhine. Heavy metals were also determined in the upper 5 cm layer of a number of floodplain areas in

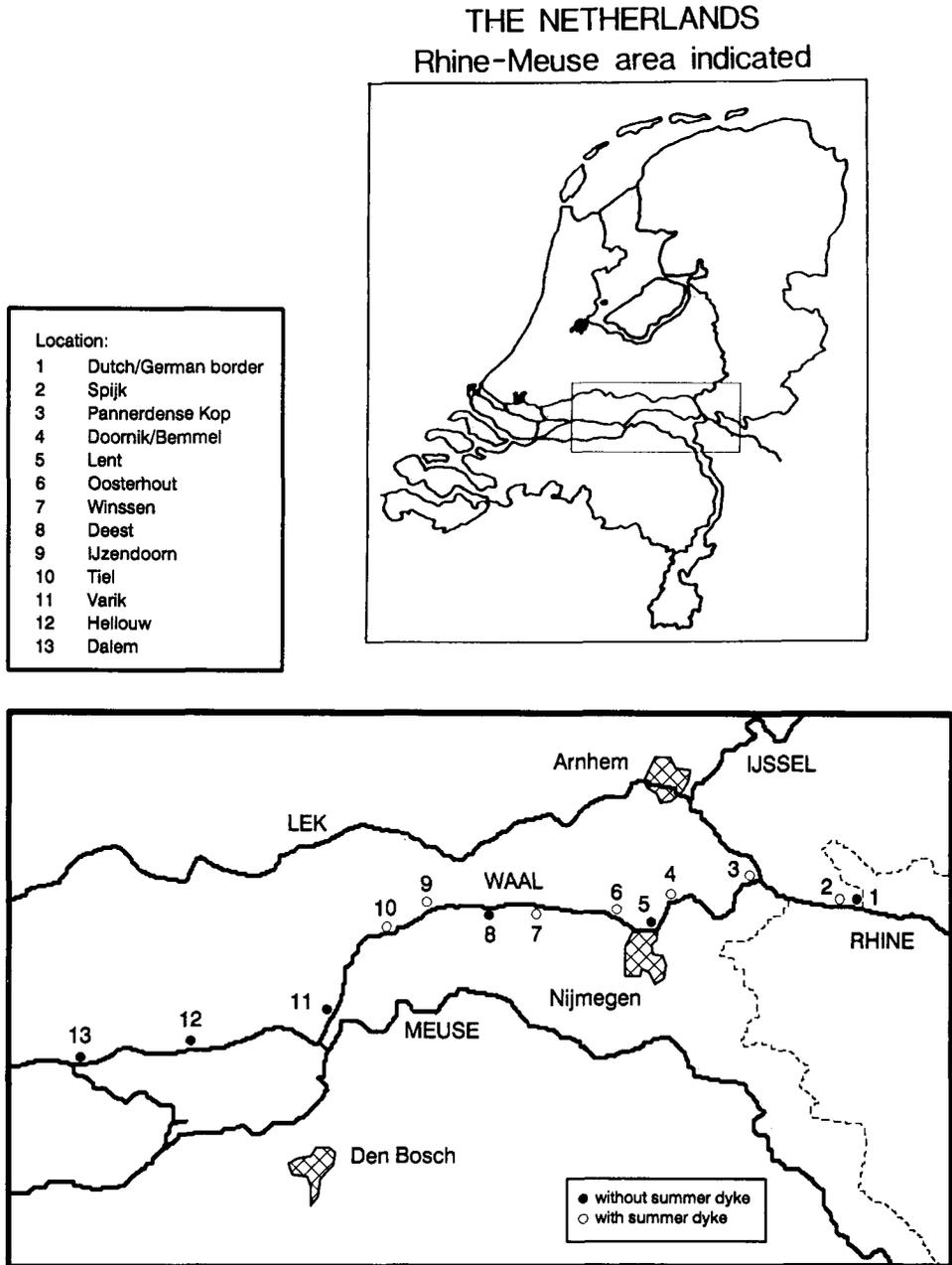


Fig. 2. Map of the Rhine river system in the Dutch lowland, indicating floodplain areas and sediment sampling sites.

Table 1. Sampling scheme for heavy metal and organic micropollutant determinations in floodplains; number of samples in every sampling year.

	Location												
	1	2	3	4	5	6	7	8	9	10	11	12	13
<i>Heavy metals</i>													
1958 (surface sample)	2	-	5	2	2	-	-	-	-	-	-	-	-
1970 (surface sample)	10	19	-	9	9	10	10	10	10	5	10	10	10
1972 (surface sample)	6	4	10	-	-	-	-	-	-	-	10	-	-
1981 (surface sample)	8	8	10	10	6	10	8	8	8	8	10	10	10
1969 (core sample)	5	2	-	5	-	-	-	-	10	10	10	10	10
<i>Organic micropollutants</i>													
1958 (surface sample)	6	-	6	2	2	-	-	-	-	-	-	-	-
1970 (surface sample)	4	4	-	4	4	-	-	-	-	4	4	-	-
1972 (surface sample)	4	4	4	-	-	-	-	-	-	-	4	-	-
1981 (surface sample)	4	4	4	4	4	-	-	-	-	4	4	-	-
1969 (core sample)	-	-	-	-	-	-	-	-	-	-	-	-	-

1969; these samples, however, did not consist of freshly settled sediment, but of a series of consecutive sediment deposits.

Organic micropollutants were determined in a smaller number of samples from only 7 locations (all included in the heavy metal analysis scheme).

Sampling took place in 1958, 1970, 1972 and 1981. It was not possible to sample all floodplain locations in every sampling year.

A survey of the samples analysed is given in Table 1.

### *Analytical procedures*

To determine the organic matter content the sample was heated with a known amount of potassium dichromate in dilute sulphuric acid. The amount of dichromate not consumed in the oxidation process was determined through titration with ferrous ion. From the amount of consumed dichromate the organic matter content was estimated.

The percentages particles  $< 2 \mu\text{m}$  and  $< 16 \mu\text{m}$  in carbonate-free mineral matter were determined by a sedimentation method based on Stokes' law (Kilmer & Alexander, 1949).

For the determination of heavy metal concentrations the dry sediments were treated with mixtures of oxidizing strong acids; depending on the element to be determined a specific acid mixture was chosen:

- Zn, Cu, Cr, Ni: hot mixture of sulphuric, nitric and perchloric acids,
- As: hot mixture of sulphuric, nitric and perchloric acids followed by treatment with hydrochloric acid/potassium iodide/ascorbic acid,

- Hg: cold mixture of sulphuric acid, nitric acid and potassium persulphate,
- Pb, Cd: hot nitric acid and final transfer to hydrochloric acid.

Analyses were carried out using flame-AAS techniques, except for As and Hg (Vierveijzer et al., 1979).

As and Hg were determined with cold AAS techniques after reduction of all chemical forms of arsenic and mercury to arsenic hydride and metallic mercury, respectively.

The analytical method for the determination of organic micropollutants has been described earlier (Japenga et al., 1987). Results are generally given as the sum of individual components:

- PAH: the sum of 6 individual PAH's (Borneff & Kunte, 1969),
- PCB: the sum of 6 congeners (numbers 28, 52, 101, 138, 153 and 180) together accounting for about 30-40 % of total PCB,
- DDT: the sum of *o,p'*- and *p,p'*-DDT and their DDD- and DDE-metabolites.

#### *Treatment of data*

Experimentally found pollutant concentrations in sediments have to be compared with reference values in order to classify the degree of pollution and to decide on possible pollution control measures. Reference values for individual pollutants were established by the Dutch authorities (Anonymous, 1987, 1988). They represent upper limits for heavy metal concentrations in soils at which all soil functions still proceed normally. Reference values were derived from the following formulas:

$$\begin{aligned}
 C'(\text{Zn}) &= C(\text{Zn}) \times 140 / [50 + 1.5 \times (2L + H)] \\
 C'(\text{Cu}) &= C(\text{Cu}) \times 36 / [15 + 0.6 \times (L + H)] \\
 C'(\text{Cr}) &= C(\text{Cr}) \times 100 / [50 + 2 \times L] \\
 C'(\text{Pb}) &= C(\text{Pb}) \times 85 / [50 + (L + H)] \\
 C'(\text{Cd}) &= C(\text{Cd}) \times 0.8 / [0.4 + 0.007(L + 3H)] \\
 C'(\text{Ni}) &= C(\text{Ni}) \times 35 / [10 + L] \\
 C'(\text{Hg}) &= C(\text{Hg}) \times 0.3 / [0.2 + 0.0017 \times (2L + H)] \\
 C'(\text{As}) &= C(\text{As}) \times 29 / [15 + 0.4 \times (L + H)]
 \end{aligned}$$

where:

- $C'$  = normalized heavy metal concentration
- $C$  = measured heavy metal concentration (mg kg<sup>-1</sup> dry matter)
- $L$  = clay content (particles < 2 μm)(%)
- $H$  = measured organic matter content (%)

To make comparisons possible, experimental data and reference values were adjusted to fit standard soil composition (25 % clay and 10 % organic matter).

By another normalization method, measured concentrations are extrapolated to material containing 50 % particles < 16 μm in the carbonate-free mineral matter. This method has been commonly used for aquatic sediments (de Groot et al., 1982). In the following paragraphs it is used only if comparison is intended with literature

data sets based on this normalization method.

Organic micropollutants are considered to be bound mainly to the organic matter fraction. Experimentally found concentrations are normalized to soil containing 10 % organic matter:

$$C' = C \times 10/H$$

where:

$C'$  = normalized organic micropollutant concentration

$C$  = measured concentration of organic micropollutant (PAH, PCB, DDT, HCB)

$H$  = measured organic matter content (%)

## Results and discussion

### *Sample characterization*

The samples varied widely in carbonate, organic matter and clay contents. Average values did not vary significantly with respect to the sampling site, but some variation between years can be observed. Average percentages (with minimum and maximum values in parentheses) are summarized in Table 2.

### *Drying procedure*

To determine whether the drying procedure used in the past caused any loss of components, a preliminary experiment was carried out. A wet sediment sample with only 1.4 % organic matter (corresponding to a low binding capacity for organic micropollutants) was analysed for PAH, PCB, DDT and HCB. The same sample was dried at 50-70 °C for 5 days and then the analyses were repeated. At temperatures below 70 °C only negligible losses occurred.

Table 2. Average contents (%) of organic matter, particles <16 µm, and calcium carbonate in river Waal floodplain sediments (minimum and maximum values in parentheses).

	Sampling year			
	1958	1970	1972	1981
Organic matter	14.5 (11.7-18.9)	11.1 (3.6-15.4)	12.3 (8.4-14.5)	10.4 (1.2-18.4)
Particles <16 µm	58.3 (38.2-72.7)	64.4 (17.4-87.2)	78.7 (28.2-88.1)	65.6 (6.9-86.2)
Calcium carbonate	13.2 (12.0-14.1)	10.2 (5.5-12.4)	12.7 (11.3-16.5)	8.7 (1.7-10.8)

As all floodplain samples were dried just after collection at 40 °C for one night and as their organic matter contents exceeded 1.4 % it can be concluded that the drying procedure did not cause any detectable loss of compounds through volatilization. Biodegradation in the air-dried sediment samples was considered negligible.

#### *Pollution levels in the period 1958-1981*

Heavy metal contents are given in Table 3 as the arithmetic mean of the concentration values corrected for clay/organic matter for all analysed floodplain sediment samples per sampling year. The 1969 core samples are included in the table; they agree quite well with the 1958-1970 fresh sediment samples. Figure 3 shows the time-course of heavy metal contamination of the river Waal floodplains; 1958 is the reference level taken as unity. To improve visualization, all samples taken in 1970 and 1972 were combined. Between 1958 and 1970/72, cadmium levels nearly doubled; copper and mercury levels increased slightly. In the same period the concentration levels of the other heavy metals decreased slightly (zinc, chromium, lead) or dramatically (arsenic); there was little change in nickel levels. After 1970/72 the concentrations of all heavy metals except nickel decreased sharply. Nickel levels remained constant during the whole period studied, which may be attributed to a mainly natural origin of nickel (this will be shown later).

Contents of organic micropollutants are given in Table 4 as the arithmetic mean of the concentration values corrected for organic matter content for all analysed floodplain sediment samples per sampling year.

Figure 4 shows the time-course of pollution levels based on the data in Table 4. In order to improve visualization, all 40 samples taken in 1970 and 1972 were combined. The values for 1958 were taken as the reference point (= 1) for the concentration changes observed.

The concentrations of PAH and DDT tended to decrease, especially after 1970/72. PCB and HCB increased substantially between 1958 and 1970/72, then decreased.

#### *Variations between floodplain locations*

Variation in heavy metal and organic micropollutant concentrations in the river Waal floodplains is much smaller when samples from one floodplain location collected in the same year are considered. It is clear that statistically significant differences exist between the locations. To find certain trends, heavy metal concentrations in relation to location characteristics were studied for two sampling years: 1970 and 1981. The reason for choosing these particular sampling years is the large number of locations sampled in these years. All locations were included except location 3 which was not sampled in 1970. It must be stressed, however, that the results given below for heavy metal levels in 1970 and 1981 are representative of all other data.

To analyse differences in concentration levels between the sampling locations the following procedure was used: average adjusted concentrations of six heavy metals (Zn, Cu, Cr, Pb, Cd, Hg) were calculated for every location in 1970 and 1981. Ni

Table 3. Average heavy metal concentrations, corrected for clay content and organic matter content, in river Waal sediments (mg kg<sup>-1</sup>). Coefficients of variation (%) are given in parentheses.

Sampling year	Number of samples	Element							
		Zn	Cu	Cr	Pb	Cd	Ni	Hg	As
1958	11	1151 (8)	146 (7)	428 (40)	303 (13)	6.4 (13)	55 (10)	5.2 (12)	87 (15)
1970	122	870 (17)	157 (24)	373 (31)	259 (19)	11.8 (27)	54 (14)	6.3 (33)	51 (21)
1972	30	1147 (9)	185 (5)	404 (22)	336 (10)	14.9 (6)	54 (9)	6.5 (16)	35 (13)
1981	114	656 (17)	104 (18)	214 (29)	173 (19)	7.5 (26)	53 (17)	1.2 (31)	24 (18)
1969 (core samples)	62	1009 (18)	184 (23)	404 (27)	277 (16)	8.9 (32)	54 (17)	7.1 (26)	58 (20)

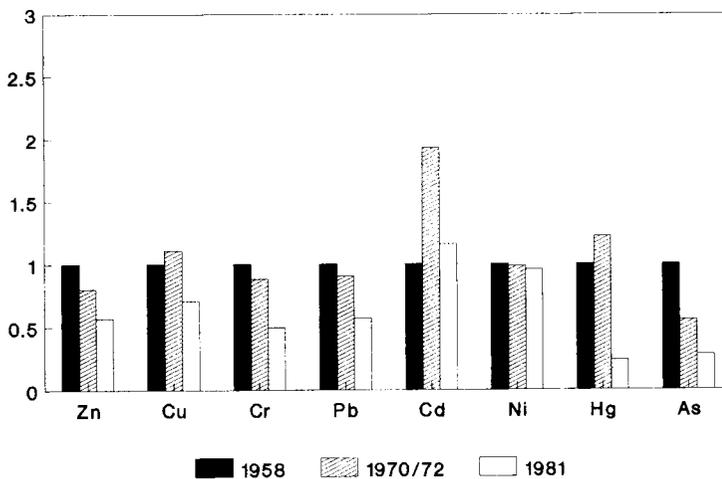


Fig. 3. Heavy metal pollution of freshly deposited sediments from the river Waal floodplains in different years (1958 = 1).

and As were not included because their concentrations were not raised due to pollution; this will be shown later. The average concentration level of each element at each location was expressed in relation to the average value of the total sample set of that element in the sampling year considered (compare Table 3). In this way the relative deviations from the annual mean were obtained for every location and for every element in the same sampling year.

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Table 4. Average organic micropollutant concentrations, corrected for organic matter content, in river Waal sediments ( $\text{mg kg}^{-1}$ ). Coefficients of variation (%) are given in parentheses.

Sampling year	Number of samples	Organic micropollutant			
		PAH	PCB	HCB	DDT
1958	16	16.8 (18)	0.49 (39)	0.14 (25)	0.28 (21)
1970	24	12.0 (38)	0.96 (47)	0.38 (46)	0.29 (30)
1972	16	13.3 (20)	0.99 (29)	0.36 (38)	0.25 (26)
1981	28	7.2 (39)	0.40 (45)	0.28 (62)	0.15 (40)

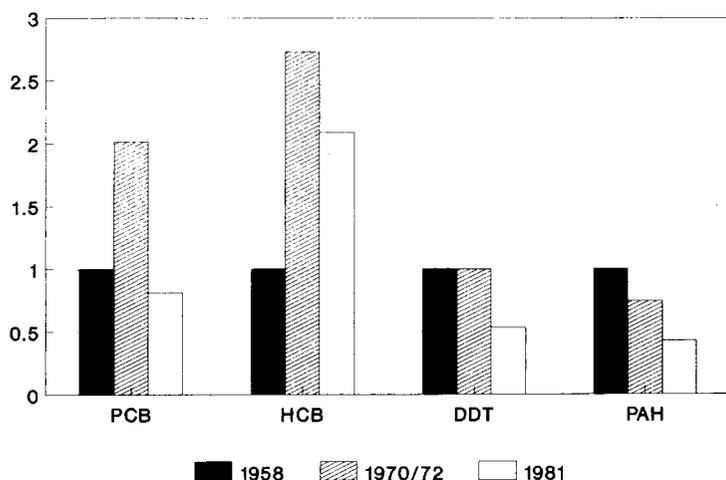


Fig. 4. Organic micropollutant pollution of freshly deposited sediments from the river Waal floodplains in different years (1958 = 1).

Figure 5 gives the variation in heavy metal contamination between locations in 1970 and 1981 (normalized to standard soil containing 25 % clay and 10 % organic matter). All elements follow more or less the same pattern (especially in 1970).

Average values for the relative deviations from the mean for all six elements (compare Fig. 5) were averaged. This gave a general value for the relative deviation from the mean for heavy metal contamination levels for all locations studied. Results are

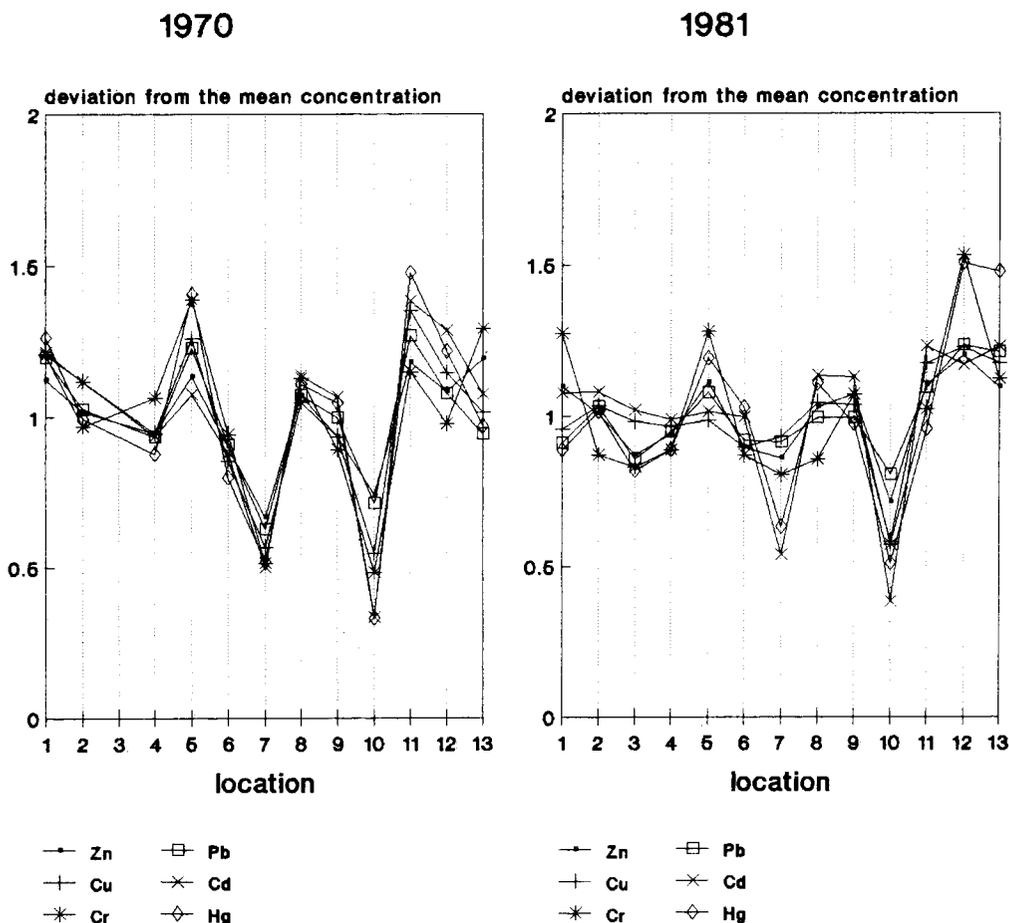


Fig. 5. Heavy metal contamination of floodplains in 1970 and 1981; variation between the locations given as relative deviations from the annual mean for individual elements.

presented in Figure 6. The locations were subdivided into two main classes: floodplains with a summer dyke and floodplains without a summer dyke. Floodplain 9 occupies an intermediate position having only a low levee instead of a summer dyke.

The results show that higher heavy metal levels in floodplains are found when a summer dyke is absent. These areas are already flooded at a moderate rise in water level; floodplains protected by summer dykes are flooded only at extremely high river discharges. This trend can be further supported by concentrations found in river sediment sampled at the Biesbosch/Nieuwe Merwede sedimentation area in 1970; here, suspended matter was deposited under average river discharge conditions and substantially higher concentration levels are found. Results for zinc and cadmium are given below (normalized to 50 % particles <math>< 16 \mu\text{m}</math>) for the three types

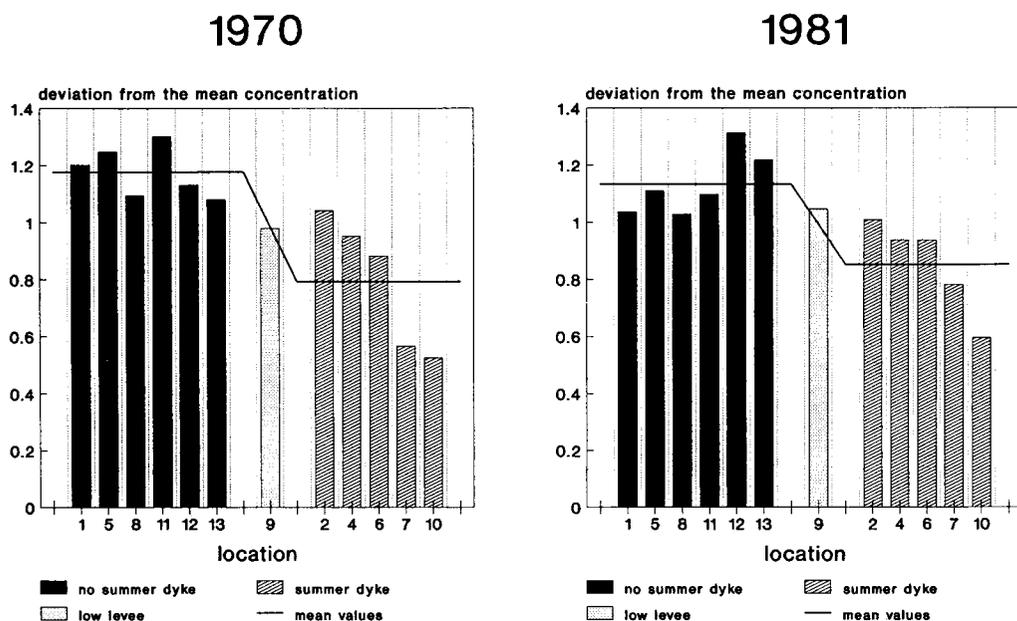


Fig. 6. Floodplain heavy metal contamination in 1970 and 1981; variation between the locations given as average relative deviations from the annual mean for all elements. The effect of summer dykes is shown.

of sediments:

— Rhine sediment (1970) (average annual water discharge):

Zn: 1855 mg kg<sup>-1</sup>, Cd: 27.1 mg kg<sup>-1</sup>

— Floodplain sediment (1970) (without summer dykes) (moderately high water discharge):

Zn: 943 mg kg<sup>-1</sup>, Cd: 12.3 mg kg<sup>-1</sup>

— Floodplain sediment (1970) (with summer dykes) (very high water discharge):

Zn: 690 mg kg<sup>-1</sup>, Cd: 7.9 mg kg<sup>-1</sup>

A clear relationship exists between water discharge and contaminant levels in the sediments: the higher the discharge the lower the heavy metal concentration levels. For suspended matter in the river Rhine this relationship was described by Salomons & Eysink (1981) (Fig. 7).

It can be concluded that the differences between floodplains protected by summer dykes and floodplains without a summer dyke shown in Figure 6 are accounted for by differences in river discharge.

#### *Classification of pollution levels*

Different methods are used for the classification of soils with respect to heavy metal contamination. Some are used as a tool to decide whether or not a soil should be

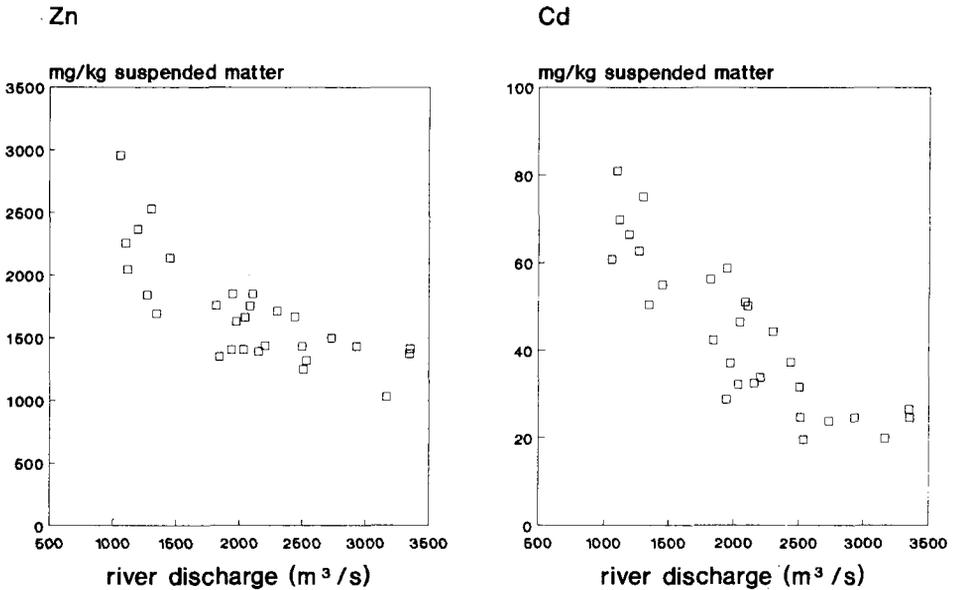


Fig. 7. Relationship between water discharge and Zn and Cd concentrations in suspended matter of the river Rhine (1977/78).

removed and cleaned. Other methods are used as an instrument for land use classification. Still other methods exist which classify the degree of pollution in relation to natural background levels.

A short outline of three different approaches is given below.

#### *Comparison with natural background levels - Igeo-values*

The experimentally found concentrations can be related to naturally occurring background levels of the heavy metals in order to determine the relative degree of contamination for each element. A straightforward classification into readily recognizable indexed groups indicating pollution severity proved to be useful. In Germany, Müller (1978) introduced a quantitative measure of the metal pollution in aquatic sediments, which is called the 'index of geoaccumulation':

$$I_{geo} = {}^2\log(C/1.5 \times B)$$

where:

*C* = the measured concentration of the element in question

*B* = the estimated background level of the element in question

Both *B* and *C* are values normalized to 50 % particles < 16 µm, because the values for background levels were expressed as such. Müller originally introduced the method for the fraction of particle size < 2 µm; the different normalization methods, however, do not give substantial differences for our data set.

The factor 1.5 in the formula is used to account for possible variations in the background levels due to lithogenic effects.

*B* is determined through the analysis of sediments deposited in the past, when little or no heavy metal contamination through human activities existed. The data sets used here are based on measurements by Salomons (1989) in sediments sampled in 1922. Other data sets give comparable background values.

Based on Igeo-values, the degree of pollution can now be classified as follows:

Igeo	Igeo pollution class	Description
>5	6	very strongly polluted
4-5	5	strongly to very strongly polluted
3-4	4	strongly polluted
2-3	3	moderately to strongly polluted
1-2	2	moderately polluted
0-1	1	unpolluted to moderately polluted
<0	0	practically unpolluted

Igeo-values were calculated using the following background values: Zn 68 mg kg<sup>-1</sup>, Cu 13 mg kg<sup>-1</sup>, Cr 72 mg kg<sup>-1</sup>, Pb 21 mg kg<sup>-1</sup>, Cd 0.25 mg kg<sup>-1</sup>, Ni 29 mg kg<sup>-1</sup>, Hg 0.1 mg kg<sup>-1</sup>, As 15 mg kg<sup>-1</sup>.

Pollution degrees based on Igeo-values are shown in Figure 8.

It can be concluded that most of the nickel present in the floodplain sediments is of natural origin. For arsenic the pollution level has decreased rapidly and the more recent floodplain sediments are practically uncontaminated with this element. Even in 1981, sediments continued to be heavily to very heavily polluted with cadmium.

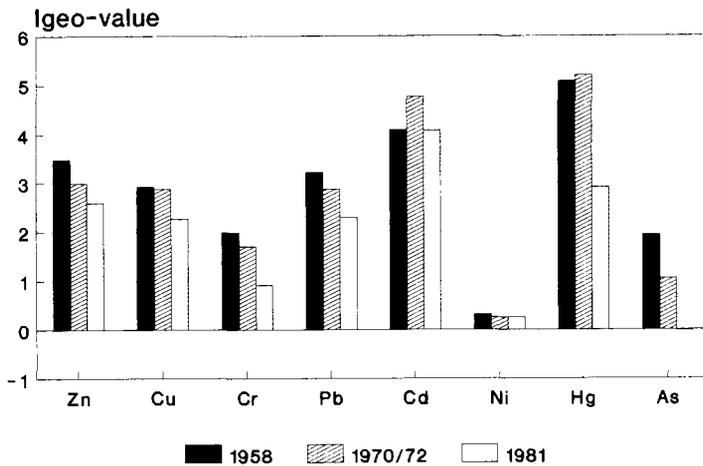


Fig. 8. Heavy metal pollution in freshly deposited sediments from the river Waal floodplains in different years, compared with natural background levels (Igeo-values).

*Comparison with reference values*

Pollution levels can also be estimated on the basis of reference values given in Table 5 (Anonymous, 1987, 1988). These values are upper limits for soils, considered to be multifunctional soils by the Dutch authorities; it means that at these heavy metal concentrations no harmful effects on organisms have been found (de Groot; pers. comm.). Reference values are used as a basis for possible source-oriented environmental protection measures to be taken by the authorities.

Figure 9a gives the proportion between the experimentally found average values (1970 and 1972 taken together to improve visualization) and the reference values from Table 5. Figure 9b shows the same values but now compared with so-called

Table 5. Heavy metal reference values R and signal values S for standard soil containing 25 % clay and 10 % organic matter (mg kg<sup>-1</sup> dry matter).

Zn	R(Zn) = 140	S(Zn) = 2500
Cu	R(Cu) = 36	S(Cu) = 400
Cr	R(Cr) = 100	S(Cr) = 600
Pb	R(Pb) = 85	S(Pb) = 700
Cd	R(Cd) = 0.8	S(Cd) = 30
Ni	R(Ni) = 35	S(Ni) = 100
Hg	R(Hg) = 0.3	S(Hg) = 15
As	R(As) = 29	S(As) = 100

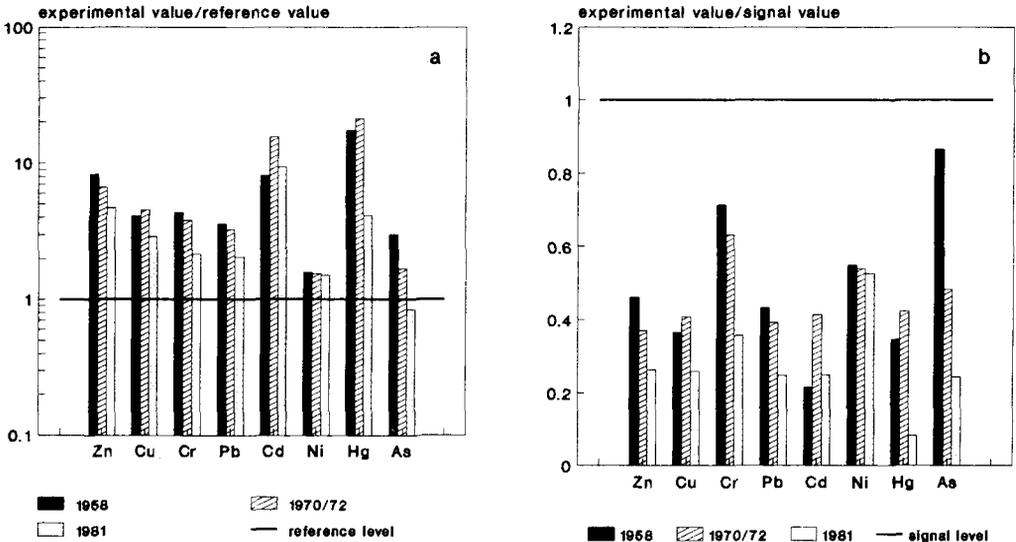


Fig. 9. Heavy metal pollution in freshly deposited sediments from the river Waal floodplains in different years, compared with reference values (a) and signal values (b).

'signal values', also given in Table 5. These values are regarded as alarm levels for sediments by the Dutch authorities (Anonymous, 1988); at such levels removal and clean-up of the soil is considered.

The figures show that the heavy metal levels generally exceed the reference values by a factor of 5 to 10; only the nickel and arsenic levels are close to the reference values. Signal values were never exceeded.

For organic micropollutants the reference values used (normalized to standard soil containing 10 % organic matter) (Anonymous, 1988) are given in Table 6. In the case of PCB's, reasonable doubt exists with respect to the given value (de Groot, pers. comm.). Figure 10a gives the ratio between the experimentally found average values (1970 and 1972 taken together) and the reference values from Table 6. Figure 10b shows the same values but now compared with so-called 'signal values'.

PCB, HCB and DDT levels exceeded the reference values by a factor of up to 100. Signal values were reached for PCB in many samples.

Table 6. Organic micropollutant reference values R and signal values S for standard soil containing 10 % organic matter (mg kg<sup>-1</sup> dry matter).

PAH	R(PAH) = 2.3	S(PAH) = 17
PCB	R(PCB) = 0.02	S(PCB) = 0.4
DDT	R(DDT) = 0.0025	S(DDT) = 0.5
HCB	R(HCB) = 0.0025	S(HCB) = 0.5

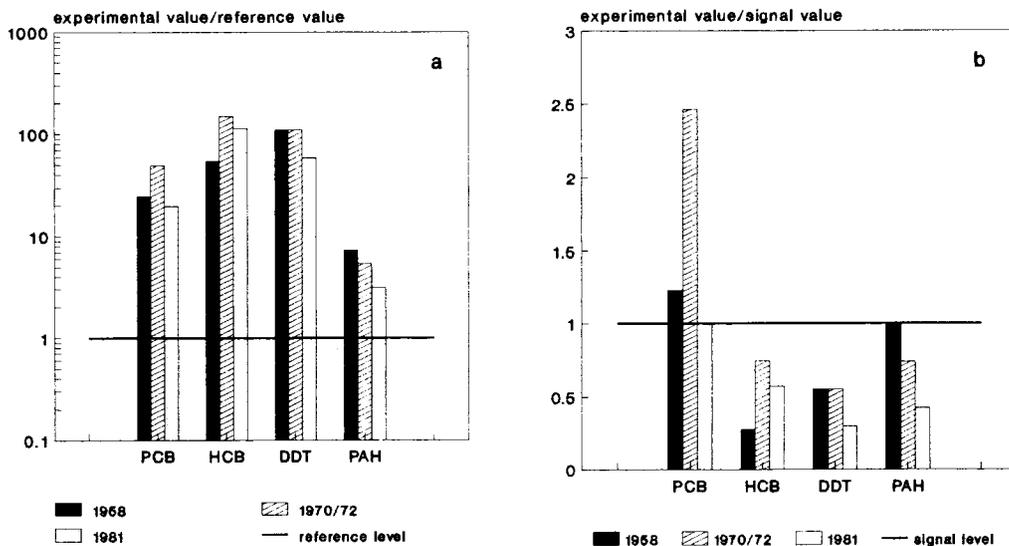


Fig. 10. Organic micropollutant pollution in freshly deposited sediments from the river Waal floodplains in different years, compared with reference values (a) and signal values (b).

### *LAC values*

The Dutch Ministry of Agriculture developed a set of values for contaminant levels in agricultural soils, the so-called LAC values (named after the technical committee which developed them) (Anonymous, 1986). These values are meant to indicate the levels above which problems might arise for plant and animal well-being or the quality of agricultural products. LAC values are dependent on soil type and land use: heavy metal availability is strongly dependent on soil composition (adsorption capacity) and on the uptake characteristics of the organisms. Because floodplain sediment deposits can be considered as clay soils used for grazing cattle and sheep, the following values are used:

- Zn: 350 mg kg<sup>-1</sup> dry matter,
- Cu: 80 mg kg<sup>-1</sup> dry matter (used for grazing cattle), 30 mg kg<sup>-1</sup> dry matter (used for grazing sheep),
- Pb: 150 mg kg<sup>-1</sup> dry matter,
- Cd: 3 mg kg<sup>-1</sup> dry matter,
- Hg: 2 mg kg<sup>-1</sup> dry matter.

The metal levels in most samples analysed were well above the LAC values. There is no evidence that cattle take in larger amounts of heavy metals when they graze in floodplains as compared with areas that are not polluted with river sediments. This might be due to the high contents of organic matter and carbonate in the floodplain sediments (van de Ven et al., 1977). Plant uptake of organic micropollutants is limited but cattle tend to consume considerable amounts of soil; milk from cattle grazing in the floodplain areas shows elevated but not alarming PCB levels (Roos et al., 1984). Eggs from birds of prey and owls living in the floodplains show increased organic micropollutant levels (Fuchs et al., 1981).

### **Conclusion**

The environmental protection measures taken during the past decades in the countries bordering the Rhine have had a measurable effect on the quality of suspended matter as reflected in the pollution of freshly deposited sediments. This is valid both for heavy metals and organic micropollutants. However, due to their immobility and chemical persistence, the pollutants described here will remain in the upper layer of the floodplain soil for many years. A real improvement of floodplain soil quality can be expected only in the next decades (if the decrease in input continues).

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