The potentials of multi-nutrient soil extraction with 0.01 M $CaCl_2$ in nutrient management

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The potentials of multi-nutrient soil extraction with 0.01 M $CaCl_2$ in nutrient management

Proefschrift

ter verkrijging van de graad van doctor

op gezag van de rector magnificus

van Wageningen Universiteit

prof. dr. ir. L. Speelman

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Stellingen

1. De ontwikkeling en implementatie van mechanistisch onderbouwde bemestingsadviezen. bestaat uit een samenhangend stappenplan; de gestandaardiseerde 0.01 M $CaCl_2$ extractiemethode is daarin een eerste en essentiële stap.
Dit proefschrift

2. De niet-gebufferde 0.01 M $BaCl_2$ grondextractiemethode (ISO 11260) leidt tot een onderschatting van de actuele CEC bij zware zavelgronden en kleigronden.
Dit proefschrift

3. Bij de huidige kortdurende teeltschema's kan de positieve invloed van het sproeien van $CaCl_2$-oplossingen op de kwaliteit van champignons niet worden verklaard door een (significante) toename van het zoutgehalte in de dekaarde.
R..B. Beelman and S. Simons. Addition of calcium chlorid to irrigation water increases calcium content and improves quality of Agraricus mushrooms independent of inherent calcium content. Mushroom Science 15: 491-497. 2000.

4. De effectiviteit van strooizout als gladheidsbestrijdingsmiddel verbetert als de hoeveelheid $CaCl_2$ ten opzichte van NaCl toeneemt.
R.C. Weast (Editor). Handbook of Chemistry and Physics. 64th Edition, CRC Press, Inc. Boca Raton, D223-D267. 1983.

5. De integratie van kennisinstellingen binnen WUR en de bijbehorende vergaande centralisatie van verantwoordelijkheden van bedrijfsactiviteiten, belemmert goed ondernemerschap van de verspreid in Nederland liggende kennisinstellingen voor praktijkonderzoek.
D. Keuning en D.J. Eppink. Verschijningsvormen van organisatiestructuren: basisvormen van organisatie nader bezien. In: Management en Organisatie; theorie en toepassing. Stenfert Kroese Uitgevers, Leiden/Antwerpen: 235-291. 1990.

6. Teeltsystemen met een gesloten nutriëntenkringloop zijn ongewenst.

7. De veelheid aan gevraagde en ongevraagde resultaten bij gebruik van multi-nutriënt analysetechnieken en multifunctionele computerrekenmodellen maakt "meten is weten" tot "meten is zweten".

Stellingen behorende bij het proefschrift:
"The potentials of multi-nutrient soil extraction with 0.01 M $CaCl_2$ in nutrient management"
P.J. van Erp, Wageningen, 12 juni 2002.

ABSTRACT

Van Erp, P.J. 2002. The potentials of multi-nutrient soil extraction with 0.01 M $CaCl_2$ in nutrient management. Doctoral Thesis, Wageningen Agricultural University, The Netherlands, 237 pages. ISBN 90-5808-664-x.

Aim of this thesis is to improve the understanding of nutrient dynamics in soil and thereby to improve decision-making in nutrient management. There is a need for a more mechanistic approach of decision-making because the classical approaches cannot comply with the tightening up of legislation and boundary conditions for sustainable agricultural production.

The thesis encompasses eight separate papers in which the mechanistic backgrounds of the 0.01 M $CaCl_2$ soil extraction procedure has been studied as well as the perspectives of the design of a multi-nutrient $CaCl_2$ soil testing program. The studies have been focussed on the cations Ca, Mg and K. Although the use of $CaCl_2$ as a soil extractant is promising, it is concluded that the design of a multi-nutrient $CaCl_2$ soil testing program is time-consuming and costly. A framework for decision-making in nutrient management has been worked out. In this framework the multi-nutrient 0.01 M $CaCl_2$ soil extraction procedure is used as a standardized procedure to give a chemical characterization of soils at a pH and ionic strength comparable to field conditions. This characterization is used as input in a soil chemical model to calculate nutrient speciation and nutrient distribution under varying conditions. This nutrient speciation and distribution is used to characterize the pool of plant available soil nutrient. It is proposed to integrate the $CaCl_2$ soil extraction procedure with a soil chemical model, a crop growth model, a soil microbiological, a soil hydraulic model and an optimization procedure into a practical tool for nutrient management decision-making. This tool can then be used i) to tune plant nutrient requirements for maximal crop production and crop quality to the magnitude of the pool of plant available soil nutrient in time and space, and ii) to optimize farm activities in order to comply with more and stricter legislation and boundary conditions related to nutrient management. It is concluded

that the perspectives of the multi-nutrient $CaCl_2$ soil extraction procedure in mechanistic soil nutrient models and in nutrient management are promising.

Key words: 0.01 M $CaCl_2$, soil testing, nutrient management, decision-making, multi-nutrient

VOORWOORD

Dit proefschrift is voor mij een afsluiting van een periode van 5 jaar waarin ik, veelal in mijn vrije tijd, de (on)mogelijkheden van 0.01 M $CaCl_2$ als grondextractiemiddel heb onderzocht. Dat ik daaraan begonnen ben, had de volgende redenen:

- de managementtaken bij mijn toenmalige werkgever Nutriënten Management Instituut NMI namen in omvang toe waardoor ik 'minder aan onderzoek en het spelen met data' toekwam wat ik ongewenst vond;
- de $CaCl_2$ extractiemethode bood mijns inziens de mogelijkheid om te komen tot een integratie van de kennisgebieden bodemchemie, bodemvruchtbaarheid, plantenvoeding & bemestingsleer, plantenfysiologie, en de modellering daarvan, waardoor de ontwikkeling van meer mechanistische bemestingsadviezen tot de mogelijkheden zou kunnen gaan behoren;
- voor het schrijven van het proefschrift zou (bijna) geen verzameling van primaire data noodzakelijk zijn: Dr. V.J.G. Houba van Wageningen Universiteit had veel analyseresultaten van relevant $CaCl_2$-onderzoek beschikbaar;
- ik had altijd al het idee om ooit een proefschrift te schrijven; en,
- door omstandigheden deed zich bij NMI de mogelijkheid voor om gedurende een beperkte periode één dag per week aan dit proefschrift te werken.

Nu het proefschrift klaar is, is het tijd om terug te kijken. Het langdurig combineren van een gezin, een verbouwing/renovatie van je huis, een fulltime baan bij NMI én het schrijven van een proefschrift, zou ik niet veel mensen willen aanraden: er zijn altijd zaken die er (on)bewust bij in schieten.

Het gedurende één dag per week aan een proefschrift werken is niet efficiënt: het is beter om er een korte tijd intensief aan te werken dan regelmatig enkele uurtjes.

Het is net niet mogelijk gebleken om het proefschrift te schrijven op basis van een bewerking van bestaande onderzoeksgegevens: voor het schrijven van het laatste manuscript moest van een aantal gronden de actuele CEC opnieuw worden bepaald. Dit

bleek een uiterst nuttige oefening omdat daarmee kon worden aangetoond dat ISO-richtlijn 11260 de actuele CEC onderschat.

Het proefschrift integreert enkele kennisgebieden. Daarmee is naar mijn mening dan ook een stap gezet op weg naar een mechanistische benadering van bodem-plant-nutriënt relaties in bemestingsadviezen. De eerlijkheid biedt te zeggen dat voordat dit werkelijk gerealiseerd kan gaan worden, nog veel onderzoek nodig zal zijn.

Het schrijven van dit proefschrift heeft er niet toe geleid dat ik mij minder met managementtaken en meer met onderzoek ben gaan bezighouden. Integendeel, sinds ik werkzaam ben als teamleider van het PPO team Paddestoelen is het 'managen' mijn hoofdtaak.

Een proefschrift schrijven doe je niet alleen: er zijn meerdere mensen die direct of indirect een bijdrage leveren aan de totstandkoming. Enkele personen wil ik hier met name noemen.

Als eerste wil ik mijn promotor Prof. Dr. Ir. O. Oenema bedanken. Oene, eigenlijk hebben we in de periode van het schrijven van het proefschrift maar weinig overleg gehad. Echter, de manuscripten van het proefschrift die ik je toestuurde, beoordeelde je snel en kritisch maar altijd opbouwend. Het is vooral in de fase van het afronden van het proefschrift geweest dat je een duidelijke stempel op het geheel hebt gezet. Je voorstel om mijn ideeën omtrent nutriëntenmanagement in een samenhangend en afsluitend hoofdstuk te formuleren heeft de afronding wel iets vertraagd maar het proefschrift mijn inziens wel verbeterd.

Dr. Ir. M.L. van Beusichem, mijn co-promotor, bedank ik voor zijn kritisch en deskundig commentaar op de verschillende manuscripten. De manuscripten met een duidelijke bodemchemische inslag ploos je helemaal uit totdat je elk symbool, formule, punt en komma begreep. In enkele conceptverhalen haalde je op deze wijze (tik)fouten uit formules of vergelijkingen. Daarnaast wil ik je bedanken voor het corrigeren van het Engels in al mijn manuscripten. Graag zou ik de samenwerking tussen ons, die begon toen NMI op de vakgroep kwam, voortzetten. Dit zal waarschijnlijk niet gaan omdat we beiden een 'andere' weg zijn ingeslagen.

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Ir. R. Pothoven, directeur van NMI, wil ik bedanken voor de mogelijkheid die hij heeft geboden om in NMI-tijd aan het proefschrift te werken. Het aanbod bleek in werkelijkheid niet altijd uitvoerbaar: regelmatig vond ik dat NMI-werkzaamheden prioriteit hadden boven het schrijven van het proefschrift. Gerard Velthof en Romke Postma wil ik bedanken voor het opvangen van bezoekers en het beantwoorden van de vele telefoontjes als ik weer eens een dag rustig aan het proefschrift wilde werken. De andere (oud) NMI-collega's wil ik bedanken voor de interesse die ze altijd hadden wat betreft de voortgang van mijn proefschrift.

Tjisse Hiemstra bedank ik voor de tijd die hij vrijmaakte als de meetdata mijn bodemchemische hypotheses niet konden bevestigen. Tjisse bedankt daarvoor.

Chris van Uffelen bedank ik voor zijn spontaan aanbod om ondanks zijn drukke werkzaamheden een groot aantal bodemchemische berekeningen voor mij uit te voeren. Jouw berekeningen hadden een grote waarde: nagenoeg alle resultaten zijn in de vorm van voorbeeldberekeningen in mijn proefschrift gekomen.

Tenslotte wil ik Pieternel, Teun en Anke bedanken voor de steun en het geduld bij de vele uren die ik thuis aan het proefschrift heb gewerkt. Ik beloof dat ik de komende tijd meer tijd voor jullie heb.

Peter van Erp

Andelst, mei 2002

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1.1 Background description

Current farm management in many developed countries is confronted with increasing demands of society and industry with respect to sustainable food production, food quality, environmental protection, nature conservation and animal welfare (FAO, 1999; European Community, 2000; FAO, 2001). These demands have resulted in legislation and boundary conditions for, among other things, the production, handling and quality of agricultural (edible) products, nutrient and pest management, use of non-renewable raw materials (e.g. De Walle and Sevenster, 1998; Sharply et al., 2000). These demands have (negative) effects on farm profitability. It is foreseen that more and stricter legislation and boundary conditions will affect farm management.

Proper nutrient management is one of the major topics in sustainable farm management, for various reasons (Van Erp and Oenema, 1993; Oenema and Pietrzak, 2002):

- it determines the crop yield and crop quality (i.e. financial crop yield);
- surplus nutrients may have negative side effects on the environment;
- non renewable raw materials are used for fertilizer production; and,
- fertilizer costs are a substantial part of total production costs.

The basic question is than 'how can nutrient management in farming systems comply with the demands of society and industry?'

It is foreseen that nutrient management has to adjust to the changing needs of market, society and industry at strategic, tactical and operational management levels. In the process of decision-making economical, environmental, legislative, agricultural and farm specific boundary conditions are integrated and profit optimized (Oenema and Pietrzak, 2002). Proper decision-making is only possible when data of the actual status of farm economics, soil, crop, labour, etc. are readily available, and when practical tools can be used that evaluate the present status and that can predict the most likelihood status after e.g. execution of farm activities, changing growing conditions, etc. This requires a good understanding of the dynamics of soil-plant-nutrient relationships.

1.2 Soil-plant-nutrient relationships

1.2.1 Four-quadrant scheme

Crop yield, crop quality and overall nutrient use efficiency, etc. are, among others, the resultant of soil and plant processes that determine nutrient availability, nutrient transport and nutrient root uptake. Detailed knowledge of (the dynamics) of these processes should be the basis for nutrient management.

The relationship between nutrient application rate and crop yield is being used for the set up of fertilizer recommendations schemes in current soil testing programs. In these schemes the optimal nutrient application rate equals the rate where the expected benefits due to yield increase equal the expected extra fertilizer costs (Cook, 1972). Since fertilizer costs are relatively low in most industrialized countries, the optimal nutrient application rate is often equal to the application rate for maximal yield. At this application rate the risk on nutrient losses to the environment is often high. Evidently, nutrient recommendation schemes should take possible nutrient losses into serious consideration.

Figure 1 depicts the four-quadrant scheme, presenting the relevant soil-plant-nutrient relationships in a soil-plant system. De Willigen and Van Noordwijk (1987) suggested to analyze fertilization experiments via this scheme and to use this scheme for the set up of more efficient fertilization strategies. Quadrant II in Figure 1 represents the relationship between the application rate of a particular nutrient and dry matter production as found in traditional fertilizer application experiments. According to the concept of the four-quadrant scheme the curve in quadrant II is the final result of the respective (basic) curves in the quadrants I, III and IV. Quadrant I describes the relationship between nutrient uptake and dry matter production. In the linear part of the curve, the nutrient is limiting dry matter production. The slope of this linear part equals the critical nutrient concentration for optimal dry matter production. This critical nutrient concentration is a plant characteristic and differs between crops and cultivars. When the curve in quadrant I levels off, other growth factors (including other nutrients) become yield limiting. This region is called the region of luxury consumption of that particular nutrient. When crop

quality is related to nutrient content, this relationship could be used to optimize crop quality. Quadrant III describes the relationship between nutrient application rate and the size of the soil pool of plant available nutrient. The pool of available nutrient consists of the amount already present and available in the soil (the intercept with the vertical axis) and the amount added by fertilization. The slope of the curve in quadrant III is not equal to 1 because not all applied nutrients are available for uptake. Part of the amount applied may get lost to the environment just after application (e.g. NH_3 volatilisation) or may not enter the available pool in the first growing season (e.g. nutrients in organic matter or P-fertilizers).

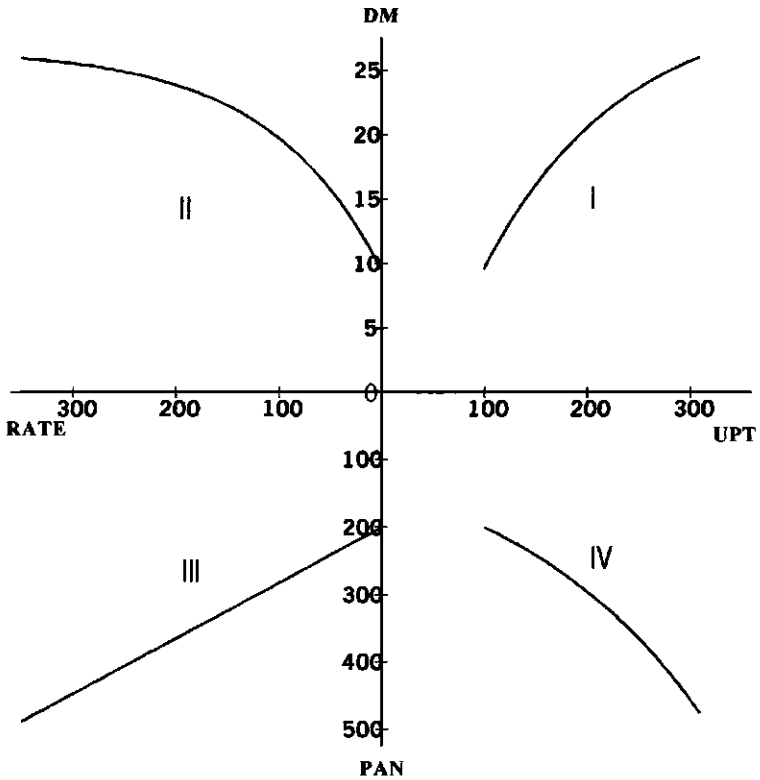

FIGURE 1. Typical example of the four-quadrant scheme. DM= dry matter yield in ton ha^{-1}, UPT= nutrient uptake in kg ha^{-1}, PAN = pool of available nutrient, in kg ha^{-1} and RATE = application rate in kg ha^{-1}

The slope of the curve in quadrant III represents the relative availability of an added nutrient source and depends on the chemical composition of the nutrient source, soil type, climatic conditions, time and method of application. The relationship in quadrant III can be used to maximize nutrient availability and overall nutrient use efficiency. Quadrant IV describes the relationship between the size of the soil pool of available nutrient and nutrient uptake. The processes in quadrant IV primarily depend on the size of the pool of the available nutrients and not on the origin of the nutrients. The curve in quadrant IV is not a 1:1 curve. Nutrient uptake from the available pool competes with processes leading to nutrient losses to the environment, for instance leaching, volatilization, denitrification. The difference between the 1:1 curve and the actual curve reflects the potential nutrient losses to the environment before, during or after the growing season. It is clear that the processes leading to the relationship in quadrant IV should be manipulated to minimize losses to the environment. The slope of the curve in quadrant IV can be interpreted as a measure for the relative depletion of the pool of available nutrients by the crop. The slope depends on e.g. the root system of the crop, the uptake capacity of the crop, and water status of the soil. Plant roots growing in soils having a low soil moisture availability, can deplete only part of the pool of available nutrient. As a result nutrient uptake is not maximal.

An increase of the overall nutrient use efficiency of agricultural systems and the concurrent decrease of nutrient losses to the environment, has to be based on improved 'sub-efficiencies' in quadrants I, III and IV. Processes in quadrants III and IV offer as much opportunity for improvement as those in quadrant I. Plant breeding may decrease critical nutrient concentrations in dry matter. However, such change may affect the nutritive value of crops and agronomic functions of the non-harvested plant residues. Efficiency in quadrant IV can be improved via a higher relative depletion by better root systems in relation to temporal and spatial aspects of nutrient availability. In quadrant III fertilizer choice and adjusting fertilization techniques to soil and climate conditions can improve nutrient use efficiency.

Summarizing, the four-quadrant scheme provides a subdivision of the basic processes involved in soil-plant-nutrient relationships. The scheme is therefore a good starting

point for integration of plant nutrient requirement for optimal crop yield and crop quality (quadrant I) and the size of the pool of (bio or) plant available nutrient (quadrants IV and III) towards a high total nutrient use efficiency and minimal nutrient losses to the environment. The (slopes of) the curves in the scheme are related to general soil characteristics like e.g. organic matter, clay content and water holding capacity and plant characteristics like critical nutrient concentrations. The soil-plant-nutrient relationships and their characteristics can be mathematically described. Therefore, the scheme has the opportunity to include general soil (and plant) characteristics in nutrient management. Basically, the relationships in the four-quadrant scheme should form the basis for nutrient management decision-making.

The definition of the pool of available nutrients is not as clear-cut as presented in Figure 1: several pools with variation in plant availability have to be distinguished. The relationships between the pool of available nutrient and nutrient availability indices as determined by current soil testing programs has been the subject of soil fertility research for decades. Currently, there is a switch from the rather empirical approach of the past, to more mechanistic approaches, as discussed further below.

1.3 Current soil testing programs

Current programs have proven their value for optimization of nutrient management in present day farming systems (Soil and Plant Analysis Council Inc., 2000). The question is whether the programs are valuable for nutrient management decision-making when the increasing demand of society and industry are taken into account. Hereafter, a comparison has been made between the desired properties of programs and the actual properties of current programs (Hergert, 1998; Benton Jones, 1998).

'Average' versus 'individual'

Farming systems will strive for maximal (financial) crop yield, optimal crop quality and maximal overall nutrient use efficiency by tuning soil nutrient availability to plant nutrient requirements in time and space. Tuning requires a precise understanding of (the dynamics of the processes underlying) soil-plant-nutrient relationships. The soil (and plant) nutrient status as determined via soil (or plant) testing programs play an important

role in these relationships. Most of the current soil testing programs treat the soil-plant-nutrient relationships rather as a black box and use a 'trial and error' method for the interpretation of soil testing data. Such approaches may be valid for determining average growing conditions, but is not applicable in site-specific and sustainable agricultural systems.

TABLE 1. Soil testing programs currently operative in The Netherlands, type of extractant and soil/solution ratio used, and the parameters needed for agricultural interpretation of the amount of nutrients extracted.

Soil testing program	Extractant	Soil/Solution ratio	Parameters needed for interpretation
pH	1 M KCl	1:5 (w/v)	Soil type, organic matter, <16 μm content, crop rotation
K, Na	0.1 M HCl +0.2 M oxalic acid	1:10 (m/v)	Soil type, organic matter, < 16 μm content, pH-KCl
Mg	0.5 M NaCl	1:5 (m/v)	Soil type, organic matter
N-mineral (NO_3 + NH_4)	1 M KCl	1:2 (v/v)	Soil type, crop
P (arable land)	Water, 20°C	1:60 (v/v)	Soil type, crop
P (grassland)	0.1 M ammonium lactate+0.4 M acetic acid (pH 3.75)	1:20 (m/v)	
B	Water, boiling	1:10 (m/v)	Crop rotation
Co	0.4 M acetic acid	1:40 (m/v)	
Cu	0.43 M HNO_3	1:10 (m/v)	Crop
Mn-reducible	1 M ammonium acetate+0.002 M hydroquinone	1:20 (m/v)	Organic matter, C/N ratio
Zn	0.4 M acetic acid	1:40 (m/v)	

'Single nutrient' versus 'all essential nutrients'

Nutrient management should take into account all nutrients essential for plant growth and their mutual interactions on fertilizer requirement. This more integrated approach is necessary to attain a combination of minimal risks on deficiencies, high overall efficiency, good crop growth, maximal crop yield and optimal crop (feeding) quality. Most of the current soil testing programs are single nutrient programs (Table 1) and the corresponding recommendation schemes seldom take into account nutrient interactions.

To analyse the soil status for all essential nutrients via common soil testing programs, numerous distinct programs will have to be executed. This is time consuming and expensive. Moreover, the results of the different programs cannot easily be linked together, mainly because of the different nature of the primary index.

'One sampling' versus 'regular monitoring'

Most of the current soil testing programs are based on the nutrient status of one 'bulked' soil sample taken just before planting or sowing. One or two nutrient applications are then recommended which aim at an'average' maximum crop yield. Nutrient management decision-making is a continuous process based on regular monitoring of the actual nutrient status of both soil and crop, on evaluation of this status, and on interpretation of this status taking well-defined boundary conditions into account. Current soil testing programs do not fit in these monitoring strategies.

Rapidity, reliability and costs

In farming systems, decision-making should be based on data of the actual soil nutrient status. Therefore, testing data should be reliable and become available rapidly after sampling. It has been shown for some of the current soil testing programs that the accuracy and repeatability is moderate. Besides, current programs have laborious procedures for sampling, sample preparation, extraction and nutrient analysis, making the execution of the programs time consuming and expensive. Therefore, current programs are not adequate to support farming systems (Houba et al., 1986).

The execution of the total package of single nutrient soil testing methods as mentioned in Table 1 cost more than 400 Euro per field. When soil testing for all nutrients is part of monitoring strategies, then the costs for soil testing will increase enormously. The costs for soil testing in monitoring strategies seem acceptable when costs are not more than 20-50 Euro per field per year. This means that costs for current programs should decrease considerably. The use of multi-nutrient extractants, e.g. 0.01 M $CaCl_2$, in combination with high tech and computerized analytical techniques are promising in decreasing soil testing costs.

1.4 Aim of the study

The (bio) availability of nutrients in soil to agricultural crops is an important growth and yield-determining factor. Currently, there is still a lack of understanding how the (bio) availability of nutrients is affected by the dynamics and interactions of processes underlying the soil-plant-nutrient relationships in agricultural soils. Mechanistic and quantitative data on the actual soil and plant nutrient status are often not readily available and there are few practical tools available that evaluate the actual status or predict future nutrient status of soil and plants. A new approach in nutrient management is therefore desirable.

The overall aim of this thesis is to improve the understanding of the availability of nutrients in soil to agricultural crops and, thereby, to improve the decision-making process in nutrient management of crop production systems. The specific objectives are as follows.

- To test and improve 0.01 M $CaCl_2$ as multi-nutrient soil extractant in soil testing programs
- To provide a sound mechanistic interpretation of the results of the multi-nutrient soil extractant 0.01 M $CaCl_2$
- To develop a conceptual framework that links results of the multi-nutrient soil extractant mechanistically to nutrient requirements of crops.

It is realized that plant testing programs as well as a good understanding of the soil physical and microbial processes in the soil-plant-nutrient relationships also contribute to a proper nutrient management. Because of a lack of time these subjects are not treated into detail in this thesis. However, integration and incorporation of these subjects in nutrient management is possible in the described conceptual framework of nutrient management decision-making.

1.5 Outline of the thesis

This thesis is a compilation of studies related to the 0.01 M $CaCl_2$ soil extraction procedure. These studies have been published in or have been submitted to scientific journals.

Chapter 2 presents the results of a study on the perspectives of using (current) soil and plant testing programs for the optimization of nutrient management.

The use of $CaCl_2$ solutions as a soil extractant is reviewed in Chapter 3. In this Chapter the perspectives of 0.01 M $CaCl_2$ as a multi-nutrient soil extractant are judged from a soil chemical, analytical and plant nutritional point of view.

The effects of soil drying temperature and the use of forced air ventilation in the drying protocol of the 0.01 M $CaCl_2$ soil extraction procedure on the amount of nutrient extracted are evaluated in Chapter 4.

In Chapter 5 a fundamental relationship is presented which relates the amount of Mg extracted by the 0.01 M $CaCl_2$ procedure to Mg extracted by conventional Mg extraction procedures. In this relationship the actual CEC is an important variable.

In Chapter 6 it is tested if the actual CEC of a soil can be estimated using pH and content of organic carbon and clay.

A study on the relationship between the pool of plant available potassium in soils and the amount of potassium extracted by the 0.01 M $BaCl_2$ method is presented in Chapter 7.

In Chapter 8 the selectivity coefficients of Ca, Mg and K exchange reactions in soils during the 0.01 M $CaCl_2$ extraction procedure are deduced. Moreover, it is tested if these coefficients can be used to obtain a reliable estimate of the amount of $BaCl_2$ extractable cations using the cationic composition of the $CaCl_2$ extract and actual CEC.

Chapter 9 evaluates the 0.01 M $BaCl_2$ soil extraction procedure (ISO 11260) as a method for the determination of the size of the cation exchange capacity and base saturation.

Finally, in Chapter 10 the main findings of this thesis are discussed and integrated into a conceptual framework for nutrient management decision-making.

1.6 Literature

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CHAPTER 2

SOIL AND PLANT TESTING PROGRAMS AS A TOOL FOR OPTIMIZING FERTILIZER STRATEGIES

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GENERAL INTRODUCTION

In order to feed the growing world population, agricultural crop production has to increase considerably. To attain this, efforts should be focussed on increasing crop yields per hectare rather than increasing the area for agricultural production (World Bank, 1992; IFA, 1995). Improvement of the fertility status of agricultural land and an economic, efficient (re-)use of mineral and organic fertilizers, organic wastes and crop residues should be promoted to achieve increases in crop yields (Smaling, 1993; Van Reuler, 1996).

Agriculture in European and North-American regions is characterized by a high crop production, a (more than) sufficient soil fertility status and a high input of nutrients via mineral and organic fertilizers (IFA, IFDC, and FAO, 1994; FAO, 1995). In these regions, agriculture is confronted with the (in)direct side effects of current management leading to nutrient losses to the environment (Isermann, 1990; Bussink, 1992; 1994), adverse effects on product quality (Breimer, 1982), high energy inputs (Fluck, 1992), production of greenhouse gases (Granli and Bøckman, 1994; Koops, Oenema, and Van Beusichem, 1996; Velthof, Brader, and Oenema, 1996), acidification (Oenema, 1990), etc.

Faced with these side effects, The Netherlands (Anonymous, 1987) and the EC (EC, 1991) proposed legislation that restricts rate, time and method of nutrient applications and the nitrogen (N) and phosphorus (P) surplus on the N and P balance sheet of farms (VROM and LNV, 1995). Its aim is to optimize nutrient-use efficiency and minimize negative side effects. To achieve compliance with an increasing amount of agricultural, environmental, legislative and economic constraints, there is a need for well-defined fertilizer strategies (Van Erp and Oenema, 1993). These strategies should lead to optimization of nutrient use, crop production and quality and at the same time satisfy the above-mentioned boundary conditions. Fertilizer strategies can be based on: (1) soil testing programs that relate nutrient availability in the rooting zone, in space and time, to crop demand (De Willigen and Van Noordwijk, 1987; Slangen, Titulaer, and Rijkers, 1989); and (2) plant testing programs that monitor crop nutrient content during growth, allowing corrective fertilizer application (Munson and Nelson, 1990).

In this chapter, the design and scientific underpinning of current soil and plant testing programs will be discussed for macronutrients and

annual field crops. The perspectives in using such programs as practical tools for optimizing fertilizer strategies will then be evaluated.

COMPONENTS OF SOIL AND PLANT TESTING PROGRAMS

There is a common agreement that 17 chemical elements are essential for metabolism, growth, development and successful reproduction of higher plants (Epstein, 1965, 1972; Brown et al., 1987; Marschner, 1995). Insight into the dynamics of nutrient availability in soil and crop nutrient requirement is necessary to optimize soil fertility status, to synchronize supply and demand and thus to maximize crop yield. Soil and plant testing programs can be useful practical tools in reaching these goals.

Soil and plant testing programs include: (1) collection and preparation of soil and plant samples; (2) chemical extraction (or pressing) of the samples; (3) determination of the nutrient concentration in the extract; (4) interpretation of the obtained nutrient concentrations in order to assess soil fertility categories or plant status categories; and (5) derivation of (corrective) fertilizer applications (Dahnke and Olson, 1990; Munson and Nelson, 1990; Peck and Soltanpour, 1990).

We define soil and plant analysis as the chemical/physical treatment of the soil or plant sample and subsequent determination of the nutrient concentration. Soil and plant analysis data provide the basis for the fertilizer recommendations, and thus form an essential part of soil and plant testing programs.

Background to Soil and Plant Analysis

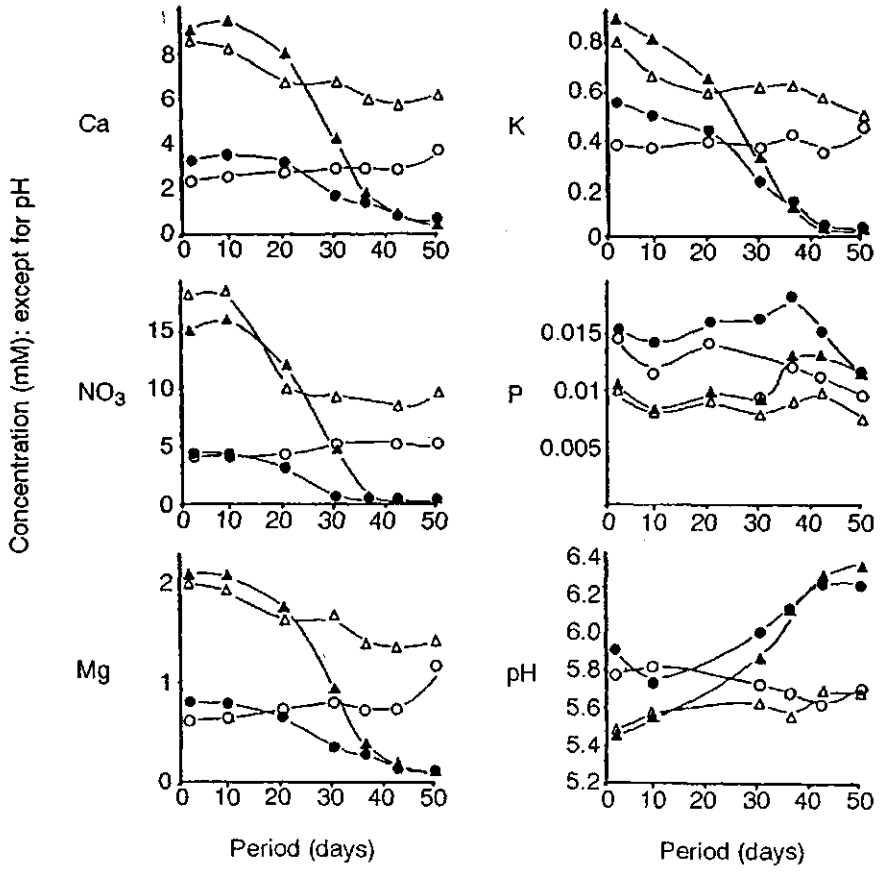
Soil Analysis

Schofield (1955) distinguished two nutrient fractions in the soil: the 'quantity,' indicating the amount of potentially available nutrients, and the 'intensity,' indicating the strength of nutrient retention. The 'quantity' reflects all the nutrients within or adsorbed at the soil constituents, whilst the 'intensity' reflects the nutrient concentration in the soil solution. The 'intensity' and 'quantity' are interrelated by the buffering capacity of the soil, which is an indicator of the capability to maintain a certain nutrient concentration in solution. The 'quanti-

ty'/'intensity' approach is valuable for nutrients like P and K (Holford, 1991; Holford and Doyle, 1992; Evangelou, Wang, and Phillips, 1994; Raven and Hossner, 1994), but cannot easily be applied to nutrients predominantly in organic forms and/or to nutrients that are hardly buffered by soil constituents. The concentration of (non-buffered) nutrients in the soil solution may vary enormously because of fertilization, nutrient uptake by crops and mineralization (Figure 1; see also Yanai et al., 1996).

Nutrient uptake rate by plant roots is considered to be positively correlated with the nutrient concentration in the soil solution (Nye and Tinker, 1977; Barber, 1984), i.e., with the 'intensity.' The nutrient

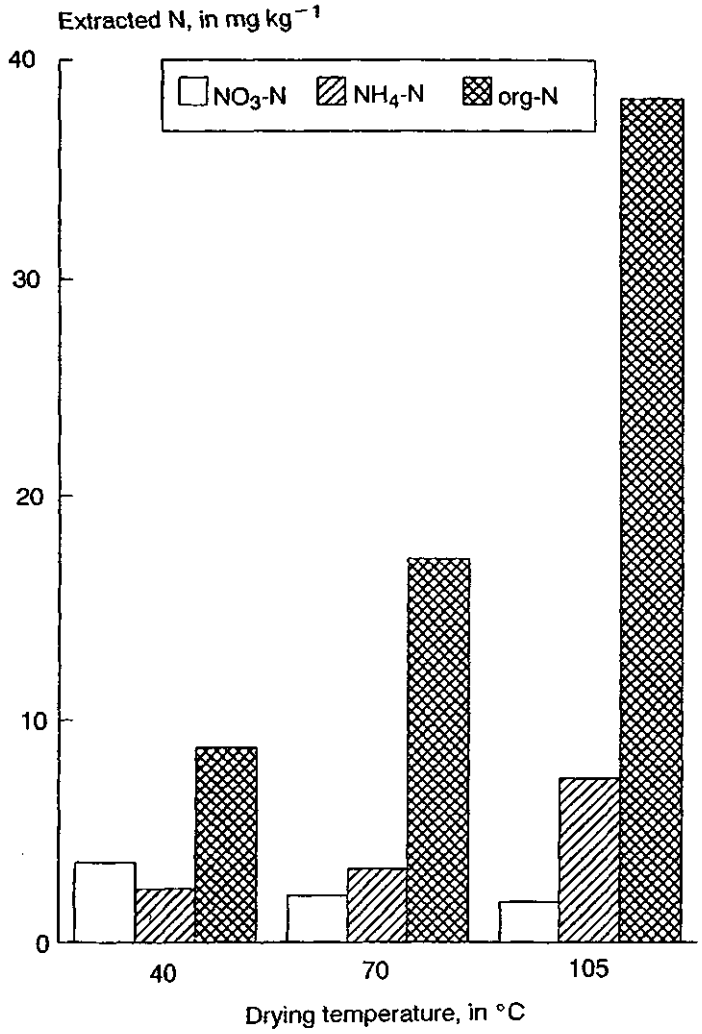
FIGURE 1. Dynamics of the concentration of Ca, NO_3, Mg, K and P as well as pH in the soil solution (Yanai et al., 1996, with kind permission from Kluwer Academic Publishers, Dordrechet, The Netherlands). ○: without N without plant, ●: without N with plant, △: with N without plant, ▲: with N with plant.



concentration in soil solution may thus be a good indicator of the actual nutrient availability in the soil. The methods available to separate the soil solution from soil constituents (Dahlgren, 1993; Jones and Edwards, 1993; Lorenz, Hamon, and McGrath, 1994; Lawrence and David, 1996) do not always provide actual concentrations because the soil solution may be altered substantially during the separation process. Nevertheless, soil extraction with water or dilute salts (Houba et al., 1990; Dahlgren, 1993) is widely used to assess the nutrient concentration in soil solution. When using these weak extractants, the amounts of extracted nutrients heavily depend on e.g., sample drying temperature (Figure 2) and sample storage (Barlett and James, 1980; Houba, Novozamsky, and Van der Lee, 1989, 1995; Rechcigl, Payne, and Sanchez, 1992), soil:solution ratio and shaking time (Rezaian et al., 1992), and extraction temperature (Houba, Novozamsky, and Van der Lee, 1989). Results of soil extraction with water or dilute salt solutions are probably related, but certainly not equal to the actual nutrient concentration in the soil solution. Interpretation/quality of soil testing programs may improve if the soil chemical processes that determine the nutrient release during the extraction process are taken into account.

Determination of the 'quantity' can be done by means of total elemental analysis. From a crop nutritional point of view, the significance of these total analyses is limited because only a very small fraction of the total reserve can be taken up by the crop during one growing period. From an agricultural point of view, estimation of the size of the 'labile' (Marschner, 1995) pool may be a better indicator of the nutrient availability. Extractants commonly used to determine this 'labile' pool are (combinations) of acids, hydroxides, complexing agents or salt solutions (Fixen and Grove, 1990; Haby, Russelle, and Skogley, 1990). Also ion-exchange resins (Rubaek and Sibbesen, 1993) or ion-exchange membranes (Qian, Schoenau, and Huang, 1992) are sometimes used to determine the size of the 'labile' nutrient pool. The theoretical foundation of the functioning of most extractants is well known, but it is difficult to use this knowledge for selecting an extractant because the chemical binding forms of nutrients in the soil are mostly unknown. Generally, nutrients associated with the cation exchange complex are extracted with high molar salt solutions (Haby, Russell, and Skogley, 1990; Meyer and Arp, 1994). Nutrients that are present in minerals with a low solubility product, or in minerals from

FIGURE 2. Effect of drying temperature on the amount of NO_3-N, NH_4-N and soluble organic N extracted with 0.01 M $CaCl_2$ (Houba, Novozamsky, and Van der Lee, 1989, with kind permission from VDLUFA, Darmstadt, Germany).



which the release is kinetically restricted, are extracted using acids or hydroxides, resins or other nutrient-specific methods (Fixen and Grove, 1990; Menon, Chien, and Chardon, 1997).

Plant Analysis

Plant nutrients are mostly taken up from the soil in an ionic form (Mengel and Kirkby, 1987). After uptake, the nutrients are distributed

throughout the plant but the major part is transported towards growing cells with an active metabolism (Marschner, 1995). Determination of the nutrient content of the whole plant is generally not a good indicator of its nutritional status because a substantial proportion of the nutrient is not metabolically active and/or incorporated in cell structures. An expanded but not fully mature leaf is metabolically very active and, therefore, it is considered that its nutritional composition may be used in the diagnosis of the nutritional state of most crops (Martin-Prével, Gagnard, and Gautier, 1987; Jones and Case, 1990; Marschner, 1995).

Advances in analytical techniques, procedures and equipment, and the increased knowledge of physiological plant nutrition have extended the development of foliar analysis as a basis of plant testing programs. In most cases, the total elemental content of the leaves is analyzed in oven-dried, ground plant material. However, extraction of plant samples with water, solutions of acetic acids, dilute HCl or a mixture of HF and HCl are also in use (Jones and Case, 1990).

Tissue testing may involve determination of the nutrient concentration in plant sap squeezed from fresh plant samples. In this way semi-quantitative information can be obtained about plant nutrients such as NO_3, HPO_4/H_2PO_4, and K (Jones and Case, 1990).

The presence or activity of enzymes or nutrient-containing metabolites may be related to the plant nutritional status (Bar-Akiva, 1971; 1984; Bouma, 1983; Hernandez et al., 1995). However, enzyme activity is not always nutrient-specific and may also be affected by plant age and external factors (Bar-Akiva, 1971, 1984; McLachlan, 1982). In addition, these techniques are labour intensive and, therefore, their usefulness in plant testing programs is limited in the short term.

Development of Soil and Plant Testing Programs

The development of soil and plant testing programs can be divided into five phases (Dahnke and Olson, 1990; Munson and Nelson, 1990): (1) formulation of soil and plant sampling strategies; (2) assessment of the correlation between the amount of nutrient extracted and crop yield or nutrient uptake; (3) ranking into soil fertility or plant status categories (= calibration); (4) interpretation of results of pot and field trials and recommendations of fertilizer rates, and (5) adjustment of the fertilizer recommendations to economic boundary conditions.

Phase 5 is an integration of phase 4 with financial boundary conditions and is beyond the scope of this work.

Sampling Strategy

A bulked soil sample needs to reflect/represent the spatial heterogeneity of the soil in an agricultural field in both horizontal and vertical directions. Numerous soil sampling procedures have been proposed for obtaining a representative soil sample from spatially heterogeneous fields (James and Wells, 1990). Similary, a plant sample needs to reflect the heterogeneity of the performance of the crop in the field and the nutritional status of a crop. Crop-specific sampling procedures have been proposed (Jones and Case, 1990). Most plant sampling procedures have an empirical basis.

Correlation Studies

Determining the best soil or plant extractant, traditionally, relies on the determination of the relationship between the concentration of the nutrient extracted and crop yield or nutrient uptake (Corey, 1987). Extractants fail when the nutrient concentration is not, or is only weakly, related to crop yield or nutrient uptake. Correlation research is usually conducted in two steps: exploratory (fertilizer) trials in the greenhouse followed by trials in the field. The advantage of pot experiments in the greenhouse is that the possible effects of the conditions in the subsoil, weather conditions and soil heterogeneity on crop yield or nutrient uptake can largely be eliminated. When an extractant is successful in greenhouse experiments, the relationship needs to be tested further in field trials because crop response is a function of many variables (Dahnke and Olson, 1990). Data of field experiments may vary because of the many factors that determine yield, e.g., soil, crop, weather, management, etc. Therefore, results of correlation analysis are often improved when relative, rather than absolute, crop yield or nutrient uptake is plotted (Dahnke and Olson, 1990; Holford and Doyle, 1992).

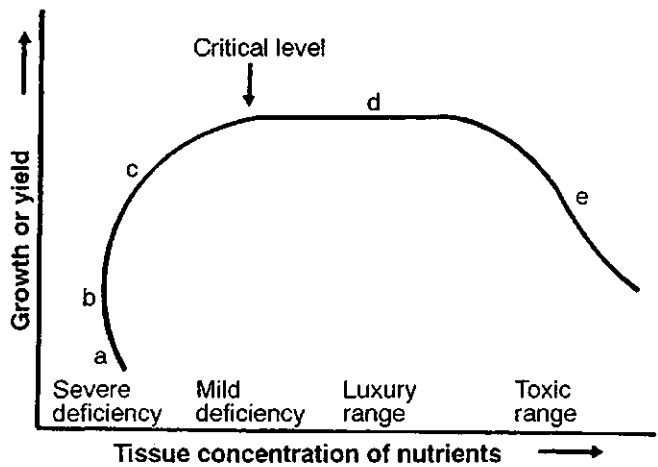
The perspectives of a newly proposed soil or plant extractant can be assessed by correlating the extraction results obtained with the new extractant to those obtained using the standard extractant (Houba et al., 1990; Matejovic and Durackova, 1994). Although this is a very useful

first-step technique in evaluating a new extractant, results need to be interpreted cautiously.

Soil Fertility Categories and Plant Status Categories

To simplify the process of making fertilizer recommendations, the results of soil and plant analysis are ranked in categories (Dahnke and Olson, 1990). A common procedure is to plot results of soil or plant analysis vs. (relative) crop response and to fit a continuous curve through the points. The curve can then be divided into soil fertility categories such as very low, low, medium, high and very high (Hauser, 1973), and plant status categories such as severe deficiency, mild deficiency, luxury range and toxic range (Figure 3; see also Smith, 1962). The basis for the division is mostly subjective and arbitrary. A more objective alternative to establish soil fertility categories is the probability approach (Fitts, 1955). This approach builds on the assumption that the results of soil analysis are not more than an indication of the crop response probability. The graphical Cate-Nelson method (Cate and Nelson, 1965) separates soils that respond from those that do not respond to added nutrients. This method has been presented as a statistical procedure that can be used to establish two or more categories (Cate and Nelson, 1971; Nelson and Anderson, 1977).

FIGURE 3. Relationship between nutrient concentration in the leaves and the growth or yield of the crop, and the division of nutrient concentrations into plant status categories (Adapted from Smith, 1962).



Interpretation of Analyses and Development of Fertilizer Recommendations

Soil Testing

In interpreting soil analytical results obtained from pot and field experiments, the relationship between the amount of nutrient extracted, the nutrient application rate and crop yield should be established. Such relationships are normally described by response models such as the linear model concept of Liebig (Waggoner and Norvell, 1979) and the curvilinear model of Mitscherlich (1928). Generally, curvilinear models are more suitable for the interpretation of field data and development of fertilization recommendations. These models, based on the 'Law of Diminishing Returns,' imply that when equal increments of a nutrient are applied to a crop, the yield response becomes smaller for each increment. This type of crop response is found in many field and pot trials. The relationship between fertilizer application and crop yield will normally be improved when soils are grouped in soil fertility categories as established by soil test calibration (Hauser, 1973). In this way, each soil fertility category has its own curve that relates nutrient application rates to crop responses.

A general criticism of curvilinear models for interpretation of field data and development of fertilizer recommendations is that in the region of near maximum yield they recommend too much fertilizer in relation to the possible increase in crop yield. In the 'Plateau yield' method (Dahnke and Olson, 1990), the relationship between fertilizer application rate and crop yield is assessed according to the linear-model concept (Waggoner and Norvell, 1979). The linear-model concept shows more clearly the application rate at which maximum yield (the plateau) is reached. From an agricultural point of view, it is logical to apply nutrients corresponding to this yield plateau.

During the 1940s and 1950s, the cation saturation ratio concept was proposed (Bear and Toth, 1948; Chu and Turk, 1949). The cation saturation ratio concept proposes ideal proportions of the major exchangeable cations in the soil. However, McLean et al. (1983) have shown that the cation saturation ratio had essentially no impact on yield.

Development of Diagnostic and Prognostic Criteria

Plant analysis may be used for either diagnosis or prognosis. For each purpose results of plant analysis need to be calibrated. Although

some promising results were obtained in developing prognostic criteria (Spencer, Jones, and Freney, 1977; Møller Nielsen, 1979a, b), the practical use in routine plant testing programs is limited. Therefore, we focus on the development of diagnostic criteria.

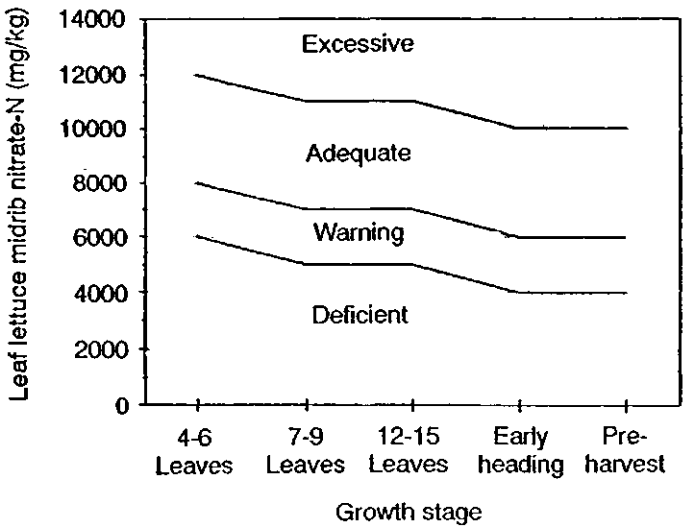
In most plant testing programs the elemental content of plant parts, e.g., fully expanded leaves, is determined to establish the nutritional status of the crop. For evaluation of that nutritional status, diagnostic criteria have been established.

Critical value. When the nutrient concentration in a plant (part) increases, the plant growth rate also increases until the so-called critical level is reached (Figure 3). Concentrations beyond the critical level do not lead to an increase in the growth rate (luxury range), and extremely high indices may even impair growth (toxic range). From an agricultural point of view, the critical level may be a valuable standard for diagnosis of the nutritional plant status (Ulrich and Hills, 1967). For many crops, critical levels have been proposed as a standard for diagnosing the nutritional plant status.

However, the critical level is not a constant; it may differ among crop varieties and is affected by e.g., nutrient interactions, water supply, temperature, dry matter yield level and physiological maturity of the leaf or plant part sampled (Bates, 1971). Moreover, determination of critical levels may lead to inaccurate values. Attempts have been made to overcome these problems by: (1) dividing plant nutrient concentrations into plant status categories (Jones, 1967); (2) defining critical nutrient ranges with the upper limit set at the critical level (Dow and Roberts, 1982); (3) using sufficiency ranges with the lower limit of the sufficient range set at about the critical level (Jones, 1967); and (4) establishing critical levels for different growth stages (Figure 4; see also Tyler and Lorenz, 1962; Pritchard, Doerge, and Thompson, 1995). Despite all these attempts, the critical level has still considerable limitations for its wide use as a diagnostic tool.

An exciting extension has been given by Webb (1972). When sufficient nutrient concentrations of a crop are plotted against crop yield, a skewed spread of points will result. The border of this spread is the maximum crop response to this concentration and is often referred to as the boundary line. For points lower than the boundary line, crop yield is considered to be restricted. The boundary line approach seems a valid way to determine the relationship between the critical level of a nutrient and crop yield. The disadvantages of this approach are: (1) the

FIGURE 4. Interpretation of leaf lettuce midrib tissue NO_3-N concentrations throughout the growth period (Pritchard, Doerge, and Thompson, 1995, with kind permission from Marcel Dekker, Inc., New York, USA).



large number of observations required, and (2) the construction of the accurate boundary line.

Nutrient ratio. Nutrient uptake and dry matter accumulation rarely proceed at equal rates in crops. Therefore, concentrations of nutrients expressed on a dry matter basis are generally not constant over time (Lorenz, Tyler, and Fullmer, 1964; Walworth and Sumner, 1988). The concentration of nutrients such as N, P, K, and S in whole plants or plant tissues tends to decrease as dry matter accumulates, while the concentration of Ca and Mg tends to increase or to remain constant (Smith, 1962; Rominger, Smith, and Peterson, 1975; Jiménez et al., 1996). Beaufils (1973) proposed using the nutrient-to-dry matter ratio to eliminate effects of dry matter accumulation.

The nutrient ratio approach has been applied to routine foliar diagnosis and forms part of the Diagnosis and Recommendation Integrated System (DRIS) (Beaufils, 1973). In DRIS, optimal nutrient ratios and the acceptable deviation from these ratios are obtained by collecting nutrient indices from healthy, high-yielding crops. Subsequently, DRIS indices are calculated for each nutrient, giving information about which nutrient is most yield-limiting and also about the order of nutrient requirement (Walworth and Sumner, 1988; Munson and Nelson,

1990). The DRIS was introduced as a universal approach for determining nutrient requirements. Nowadays, its value is debated since it appears a relatively site-specific approach (Beverly, 1993; Baldock and Schulte, 1996). Baldock and Schulte (1996) proposed PASS (Plant Analysis with Standarized Scores) for interpretation of plant analysis. PASS is a combination of the sufficiency range approach and DRIS.

Alternatives. Prevot and Ollagnier (1961a, b) estimated the relative proportions of (interacting) nutrients in plants, which should result in balanced plant growth. Kenworthy (1967, 1973) proposed generating nutrient optima by averaging tissue values of healthy crops rather than by determination of critical values from crop response studies. Møller Nielsen (1971) proposed a system which addresses problems associated with plant physiological age and nutrient interactions. Although the approach is innovative, the amount of data necessary to work out this concept is extremely large and therefore not very promising for wide application in agriculture.

CRITICAL EVALUATION OF SOIL AND PLANT TESTING PROGRAMS

Collection of Soil Samples

Agricultural fields are variable in the horizontal and vertical direction because of natural variation, e.g., soil forming processes (Finke, Bouma, and Stein, 1992), and human influences, e.g., row application of fertilizers (Hofman et al., 1993). Soil sampling schemes should take into account this variability in order to obtain representative analytical data and to develop adequate soil testing programs (Peck and Soltanpour, 1990). Different soil sampling strategies have been proposed to obtain samples which accurately reflect the whole field's nutrient status or parts of it (Kitchen, Havlin, and Westfall, 1990; Mahler, 1990; Entz and Chang, 1991; Blair and Lefroy, 1993; James and Hurst, 1995).

Most current soil testing programs, fertilizer recommendations and fertilizer application techniques aim at one homogeneous application per field. This approach seems inadequate for non-homogeneous fields because it may lead to underdosage or overdosage of fertilizers, resulting in reductions of crop yield and crop quality or in nutrient

losses to the environment. When variability is large, knowledge of the spatial variability in combination with site-specific fertilizer application techniques are promising tools to adjust nutrient availability to plant demand and to reduce the risk of losses to the environment (Robert, Rust, and Larson, 1996).

Traditionally, soil samples are taken from the 5 to 30 cm top layer of agricultural soils, mainly because the major portion of the root system is in this layer (De Willigen and Van Noordwijk, 1987). However, crops can take up considerable amounts of nutrients from the subsoil (Kuhlmann and Baumgartel, 1991). This holds true especially for nutrients like K, NO_3 and SO_4 under conditions where the precipitation surplus is small and drainage rarely occurs. Soil testing programs can be improved by estimating the soil's nutrient reserves to a depth related to the rooting zone (Neeteson, 1989).

Most present day soil testing programs aim at collecting one soil sample per year for 'mobile' nutrients and one soil sample per crop rotation (3-6 years) for 'immobile' nutrients. This seems tricky because soil fertility status may show considerable seasonal variation (Espinoza et al., 1991; Carr and Ritchie, 1993). We think that the sampling frequency of present day soil programs is far from sufficient for strategies that aim at fine-tuning of soil nutrient availability to plant demand. Regular soil analysis during the growing season should become an essential part of these strategies, especially for nutrients which are not well buffered in soils.

Collection of Plant Samples

The nutrient content of a plant is not a fixed entity, but varies from month to month, day to day and even from hour to hour as well as between plant organs. Plant sampling schemes should be adapted to this variability in order to be a true and accurate tool for monitoring the crop nutrient concentration (Bolland, 1995). In general, organs that are physiologically young and are subject to rapid changes in nutritional concentration, and organs that have passed full maturity should not be sampled (Bouma, 1983; Jones and Case, 1990; Ernst, 1995). After a period of stress due to possible nutritional deficiency or imbalance, crops develop unusual nutrient concentrations which can lead to serious misinterpretation of the nutritional status. The necessity for standardization of sampling techniques and protocols cannot be overemphasized (Farina, 1994), since current criteria for the interpretation

of plant analysis data have been established for well-defined conditions only.

Extraction Procedures

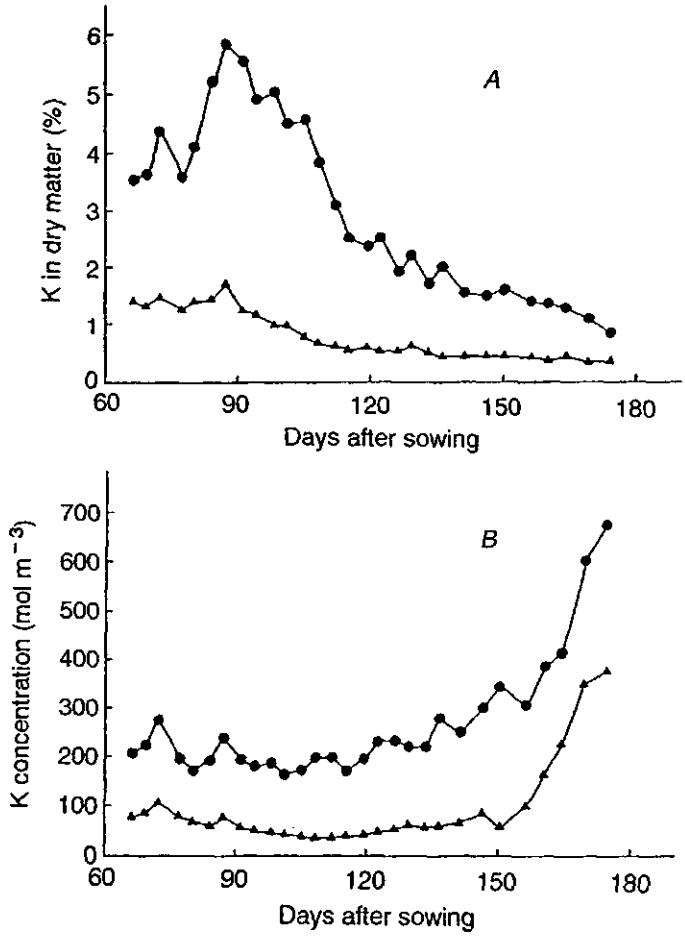
The chemical extraction of a soil or plant sample and subsequent determination of the nutrient concentration in the extract is the basis of soil and plant testing programs. If analytical procedures are carried out under well-defined conditions, reproducibility and accuracy is generally very high. The protocols should at least contain information on sample preparation (drying temperature, duration of drying, mixing), extraction conditions (temperature, soil-to-solution ratio, shaking time, method of separation of soil or plant material from extractant, etc.), and the use of reference or certified soil samples.

Interpretation of Plant Nutrient Concentrations

It is routine in most laboratories to express nutrient concentrations in plant material on a dry matter basis. This has some advantages because dry matter is a measure of crop biomass that will not change much with post harvest treatments. However, it is found that nutrient concentrations expressed on a dry matter basis vary with time; concentrations are mostly high in young plants and decline during ageing (Smith, 1962). It is, therefore, not very useful to define a 'critical' concentration that is required for maximum growth without making a clear reference to the developmental stage at sampling. When nutrient concentrations are expressed on a dry matter basis, the fact that the physiological activity of a nutrient is related to its concentration in the aqueous phase is ignored. More accurate insight into the plant nutritional status may therefore be obtained by expressing concentrations relative to water content. Leigh and Johnston (1983a, b) have shown that leaves of barley adequately supplied with K had more or less constant K concentrations relative to water content throughout vegetative and early reproductive growth, while the concentration based on dry matter declined during growth (Figure 5). This concept is also useful for nitrogen (Leigh and Johnston, 1985).

The total nutrient concentration of a plant part does not always give an indication of the physiological nutrient activity. Analysis of plant sap, as is the case with organ testing, may improve the diagnostic

FIGURE 5. Time-dependent changes in the concentration of K in shoots of barley, expressed on the basis of (A) dry matter and (B) tissue water. Exchangeable K concentrations of the soils were 382 (●) or 55 (▲) mg kg^{-1} dry soil, respectively (Leigh and Storey, 1991, with kind permission from Cambridge University Press, Cambridge, UK).



value of the nutrient concentrations obtained. Nutrients in plant organs can be heterogeneously distributed between cell types. This distribution may have implications for the interpretation of nutrient concentrations in plant organs. The nutrient concentration of whole organs has little validity concerning physiological status of the composing cell types. On the intracellular level, nutrients are distributed between the cytoplasm and the vacuole. The cytoplasm and its organelles represent the site of most metabolic processes, and the nutrient composition and the nutrient concentrations should remain more or less constant in a

certain developmental stage. Physiological nutrient shortages of N, P and K appear to be largely influenced by cytoplasmic nutrient concentrations (Mengel and Kirkby, 1987; Marschner, 1995). Nutrients present in the vacuole, such as K, contribute to the osmotic potential (Leigh and Wyn Jones, 1984) but have no unique or essential role in the vacuole. Providing that other solutes are available to maintain turgescence (Pitman, Mowat, and Nair, 1971), the concentration of any nutrient in the vacuole, and thus in the cells or plant organs as a whole, may vary with supply. This explains why the critical concentration of K in plant tissue is affected by the availability of cations like Na, Mg and Ca (Leigh and Storey, 1991).

From the above considerations it is clear that total nutrient concentrations in plant organs have little, if any, plant physiological meaning. Despite this, total nutrient concentrations in plant testing programs that are properly calibrated may be correlated to the plant nutritional status.

Interpretation of Soil Extractable Nutrients

In the soil, nutrients are retained in many chemical forms. The absolute or relative amount of a nutrient that is released during extraction depends on the total amount present, on the distribution over the different chemical binding forms, and on the extracting power of the extractant. There is generally an enormous discrepancy between the amount of nutrient extracted and actual nutrient uptake by crops. Furthermore, nutrient uptake by the same crop may vary between years and different crops may take up different amounts of nutrients from the same soil (Yerokun and Christenson, 1990; Schoenau and Huang, 1991; Smith and Li, 1993). The mode of action of many soil extractants when brought into contact with the soil sample is still largely unknown. At present, many extractants are in use for the assessment of a single-element fertility status of the soils. When different extractants are applied to the same soil, the amount of extractable nutrients may differ enormously (Matejovic and Durackova, 1994).

Crop Yield

Soil and plant testing programs are correlated, calibrated and interpreted with crop yield as the determinant (Dahnke and Olson, 1990;

Munson and Nelson, 1990; Blair and Lefroy, 1993). When crop yields of many field trials are plotted against a single independent variable, e.g., soil fertility or plant nutrient content, a spread of points will result because under field conditions other independent variables may also change (Webb, 1972; Walworth, Letzsch, and Sumner, 1986). The maximum response to an independent variable is the border of the spread of points, but the majority of the fields have crop yields below this border. In all these cases, factors other than nutrient availability have determined actual crop yield. The dependence of crop yield on other factors indicates that soil and plant testing programs need more background research on the contribution of these factors to crop yield before fertilization can be optimized on a field scale.

Fertilizer Application and Crop Response

There is a relationship between soil fertility status, fertilizer application rate and crop response. To achieve the desired crop yield, the fertilizer application rate on soils with a low fertility status should be higher than on soils with a higher fertility status. There is, however, no single relationship which can be used to describe changes in plant nutrient concentration upon addition of fertilizer. Thus, foliar diagnosis alone cannot be used to determine how much fertilizer to add, or to predict accurately crop response to added fertilizer in any given situation. These relationships are largely affected by non-nutritional factors, and further in-depth research is necessary before they can be incorporated successfully in future fertilizer recommendations (Walworth and Sumner, 1988; Beverly, 1993; Marschner, 1995).

Environmental Side-Effects Related to Soil Testing Programs

Most soil testing programs have been calibrated under a wide diversity of field conditions. These programs are currently a useful practical tool to match the fertilizer application rate with the soil fertility status, the crop yield target, and crop quality, and at the same time to achieve the sufficient soil fertility status. The recommended application rates will generally lead to relatively high nutrient-use efficiencies. When fertilizer application exceeds the recommended rates, nutrients will certainly be left in the soil profile at harvest. The 'mobile' nutrients are then subject to leaching during a period of precipitation surplus, while

the 'immobile' nutrients may remain in the rooting zone of the soil profile and increase the soil fertility status. When subsequent fertilizer application rates are not adjusted to the enhanced soil fertility status, the risk of nutrient losses through leaching, denitrification or surface run-off may increase accordingly.

Most fertilizer recommendation schemes have been developed from fertilizer field trials on well-defined fields where water-soluble single nutrient fertilizers with a well-known composition had been broadcast and further incorporated in the soil just before sowing or planting. If these experimental boundary conditions are not taken into account during the practical application of fertilizers, fertilization according to the recommendation schemes may lead to considerable environmental side-effects or decreased nutrient availability. Use of multi-nutrient fertilizer generally leads to under or overdosage of more than one nutrient.

To increase nutrient use efficiency and to alleviate side-effects of fertilization, soil testing programs should also provide information on the impact of choice of fertilizer (e.g., inorganic versus organic forms) and on timing and methods of application. Application of fertilizers long before planting or sowing may result in leaching and/or denitrification losses (Addiscott, Whitmore, and Powlson, 1991). Surface application of ammonium-containing fertilizers on carbonate-containing soils and of urea-containing fertilizers on all soil types may lead to ammonia volatilization. Injection or direct incorporation of these fertilizers in the top layer of soil decreases ammonia volatilization (Hargrove, 1988). Broadcast application of water-soluble P and K fertilizers on P- or K-fixing soils, respectively, may result in decreased P or K availability to crops (Tingre et al., 1992). Banding just before sowing or planting may then improve the plant availability of applied P and K (Knittel, 1988).

EVALUATION

Thus far, the basis of most soil and plant testing programs is the statistical relationship between the concentration of one or more extracted plant nutrients and crop response. Since many factors determine crop response, the relationships are frequently not very strong and, moreover, site and crop specific. Despite the empirical and site-specific approach of most plant and soil testing programs, they are still

the best tools available to optimize fertilizer strategies under these specific conditions. The testing programs are effective, especially when (soil) nutrient availability is the major factor restricting crop response.

In European and North-American regions, agriculture is confronted with an increasing number of agricultural, environmental, economic and legislative boundary conditions that restrict fertilizer use. To satisfy these demands and constraints, fertilizer strategies like Integrated Nutrient Management (Van Erp and Oenema, 1993) and Balanced Fertilization (Steen, 1996) have been proposed. Integrated Nutrient Management (INM) seems most realistic from an agricultural point of view and aims at monitoring and steering of nutrient flows in the soil-plant system. Computorized crop growing models and quantitative risk analysis techniques may be helpful tools to estimate fertilizer requirements and the probability of responses. The use of multi-nutrient extractants should be promoted to reduce the number of soil analyses.

For INM, a more scientific approach of soil and plant testing programs will be unavoidable. Therefore, future soil and plant testing programs should focus on the extraction and determination of nutrient (fractions) that are related to relevant soil and plant processes and can be used in crop growing models.

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CHAPTER 3

ONE HUNDREDTH MOLAR CALCIUM CHLORIDE EXTRACTION PROCEDURE. PART I: A REVIEW OF SOIL CHEMICAL, ANALYTICAL AND PLANT NUTRITIONAL ASPECTS

P.J. Van Erp, V.J.G. Houba and M.L. Van Beusichem (1998)

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ONE HUNDREDTH MOLAR CALCIUM CHLORID EXTRACTION PROCEDURE. PART I: A REVIEW OF SOIL CHEMICAL, ANALYTICAL, AND PLANT NUTRITIONAL ASPECTS

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ABSTRACT

The economical and operational aspects of multi-nutrient extractants make them attractive for soil testing programs. However, the value of a multi-nutrient extractant is primarily determined by the relationship between the amount of nutrient extracted and crop response. To determine the perspectives of the 0.01 M $CaCl_2$ extraction procedure as a multi-nutrient extractant, this paper reviews literature on the soil chemical, analytical and plant nutritional aspects of $CaCl_2$ solutions as a soil extractant. Recent decades, $CaCl_2$ solutions were common single nutrient extractants in plant nutritional and soil chemical research but the amount of nutrient extracted was sensitive for differences in sample treatment and extraction procedure. Therefore, a 0.01 M $CaCl_2$ procedure should be standardized to obtain a robust procedure. Calibration studies between conventional soil extraction procedure and the 0.01 M $CaCl_2$ procedure show fairly good relationships. A first step to develop a multi-nutrient 0.01 M $CaCl_2$ soil testing program is to convert conventional soil testing programs into 0.01 M $CaCl_2$ programs based on these relationships. Validation of these programs with pot and field experiments remains necessary. Further research is suggested to test if the 'labile' pool of plant nutrients in a soil can be estimated based on the pH, the composition of the supernatant and soil characteristics. It is concluded that the 0.01 M $CaCl_2$ procedure is a promising tool in near future farm nutrient management.

INTRODUCTION

Plant roots take up plant nutrients from the soil. To obtain a good crop growth, crop yield and crop quality, soil nutrient availability should at least equal crop demand. In soil testing programs the soil nutrient status and recommended nutrient application rate are defined after soil extraction with chemicals. Most of these soil testing programs are single nutrient programs which are laborious, expensive and have a high use of chemicals. Multi-nutrient soil testing programs are attractive from a laboratory point of view because of the economical and operational advantages. In 1986, Houba et al. [32] proposed the 0.01 M $CaCl_2$ procedure as a multi-nutrient soil extractant. In the 0.01 M $CaCl_2$ procedure, fresh soil is dried in the air or at 40°C in a drying oven with forced air ventilation. After crushing and sieving, the fraction < 2 mm is shaken (end-over-end or horizontally) during two hours at 20°C with 0.01 M $CaCl_2$ of 20°C in an extraction ratio of 1:10 (weight to volume). After measurement of the pH in the settling suspension, the suspension is centrifuged at about 2,000 g. Analytical techniques for the determination (simultaneously) of organic carbon (C_{org}), nitrate (NO_3), ammonium (NH_4), nitrogen (N), ortho-phosphate (P_{ortho}), phosphorus (P), sulphate (SO_4), sulphur (S), aluminium (Al), iron (Fe), boron (B), sodium (Na), potassium (K), magnesium (Mg), cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), zinc (Zn) and polyphenols are worked out [39]. The extracted nutrients are expressed in mg kg^{-1} dry soil. Analytical techniques for other elements or element fractions will become available in the near future.

In recent years, the 0.01 M $CaCl_2$ procedure has received a lot of attention because of the good relationship among nutrients extracted with the 0.01 M $CaCl_2$ procedure and conventional soil extraction procedures [32] and the economical and operational aspects which are attractive from a laboratory point of view. The aim of this paper is to determine the perspectives of the multi-nutrient 0.01 M $CaCl_2$ procedure based on a literature review of soil chemical, analytical and plant nutritional aspects of $CaCl_2$ solutions as a soil extractant.

Effects of soil drying and drying temperature

Dried soil samples simplify optimization and automation of activities in the laboratory. However, soil drying may have a drastic effect on the extractability of many nutrients [4,12,13,65,67,79]. Houba et al. [33] found that, on average, soil drying and drying temperature increased the amount of 0.01 M $CaCl_2$-extractable NO_3, NH_4 and N_{org} (Table 1), and Hylander et al. [44] found an effect of soil drying on the amount of 0.01 M $CaCl_2$ extractable P and P_{ortho}.

TABLE 1. Effect of drying and drying temperature (°C) on the amount of 0.01 M $CaCl_2$ extractable nitrate (NO_3-N), ammonium (NH_4-N) and soluble organic N (N_{org}) in six different soils, in mg kg^{-1} [33]

soil number	NO_3-N			NH_4-N			N_{org}		
	fresh	40°C	105°C	fresh	40°C	105°C	fresh	40°C	105°C
1	20.8	24.6	22.1	1.9	3.9	12.4	3.1	6.9	26.5
2	4.6	3.6	1.8	1.8	2.4	7.4	2.2	8.8	38.2
3	5.8	6.7	6.2	0.0	1.7	5.9	1.8	2.2	13.3
4	8.6	9.5	5.6	0.2	3.7	23.2	5.6	18.5	108.9
5	9.6	10.9	8.8	1.2	1.8	9.1	5.2	16.4	90.4
6	0.6	0.3	0.5	2.0	3.7	8.6	2.1	10.4	19.2

The effect of drying and drying temperature on the amount of 0.01 M $CaCl_2$ extractable nutrients may lead to a misinterpretation of the soil nutrient status under field conditions. Therefore, further research is necessary to compare and quantify the effect of soil drying and drying temperature on the amount of 0.01 M $CaCl_2$ extractable nutrients.

Effect of grinding

In most soil extraction procedures a small subsample is taken from a dried, crushed and ground soil sample. A soil sample is crushed and ground to ensure that a representative subsample is taken. Houba et al. [34] have found that pH and extractable K, Mn, Na and NH_4 determined by a 0.01 M $CaCl_2$ extraction are significantly influenced by the degree of grinding. The study suggests that the effect of grinding on the amount of extractable nutrients is larger for weak extractants. This effect of grinding underlines the need for standardization of the grinding procedure in a 0.01 M $CaCl_2$ procedure.

Effect of soil-solution ratio

The effect of the soil-solution ratio on the amount of extractable NO_3-N, P_{ortho} and K is shown for an agricultural soil in Figure 1.

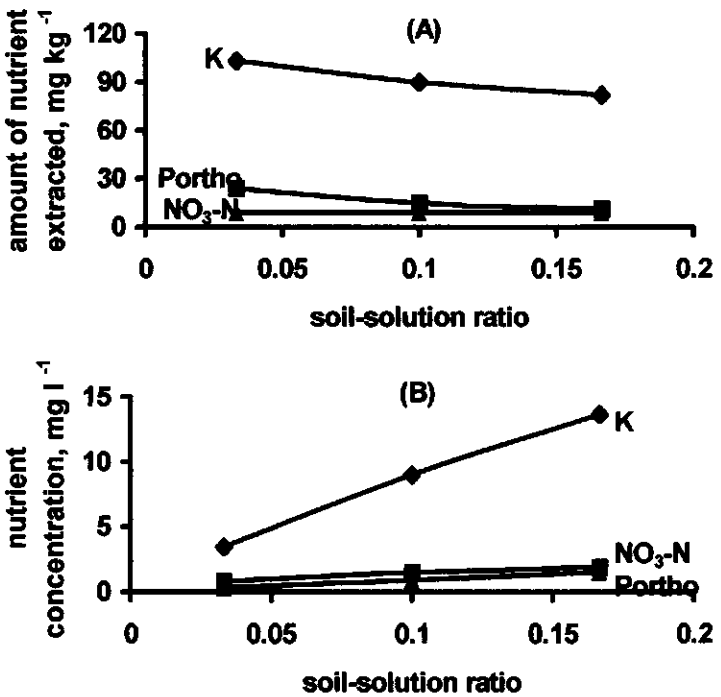

FIGURE 1. Effect of soil-solution ratio on the total amount of extractable ortho-phosphate (P_{ortho}), potassium (K) and nitrate (NO_3-N) (A) and the concentration of P_{ortho}, K and NO_3-N in the solution (B). Unpublished results of a sand soil.

The soil-solution ratio has no effect on the total amount of extractable NO_3-N but the NO_3-N concentration in the soil suspension is proportional to the soil-solution ratio. This effect is found in most soils and shows that NO_3-N is not or almost not buffered by soil particles. The total amount of extractable P_{ortho} and K increases and the P_{ortho} and K concentration in the soil suspension decreased when the soil-solution ratio decreases. The decrease in P_{ortho} and K concentration is not proportional to soil-solution ratio. This means that the P_{ortho} and K concentrations are buffered by the soil particles. Similar effects have been found for P_{ortho} by Wild [90] and Bendi and Gilkes [14], for K by Bijay Singh et al. [15] and for Mg by Schachtschabel [70]. The indicated effects of soil-solution ratio on extractable nutrients are also found for other soil extractants [83]. The effect of soil-solution ratio on pH measurement in 0.01 M $CaCl_2$ is limited [11] because buffering capacity for hydrogen of most soils is large. The effect of soil-solution ratio on the amount of extractable nutrients necessitates standardization of the soil-solution ratio in the 0.01 M $CaCl_2$ procedure.

Effect of extraction period

The within laboratory variation (repeatability) and between laboratory variation (reproducibility) of an extraction procedure will improve when deviations in e.g. extraction period have no significant effect on the total amount of extractable nutrients. Extraction of the nutrients Mg, Na, K, NO_3, NH_4, N and P_{ortho} during a 0.01 M $CaCl_2$ extraction is a kinetically fast process (Figure 2). When the amount of nutrients extracted after 2 hours is expressed as a percentage of the amount extracted after 4 hours, than more than 96 percent has been extracted, on average. Between soils, differences may exist. The amount of extractable nutrients is more or less constant after a 2 hours extraction period, except for P_{ortho}. Wild [90] also found that P_{ortho} concentrations decreased when extraction period increased. From this it can be concluded that in a 0.01 M $CaCl_2$ procedure an extraction period of two hours seems sufficient for an almost complete extraction of nutrients.

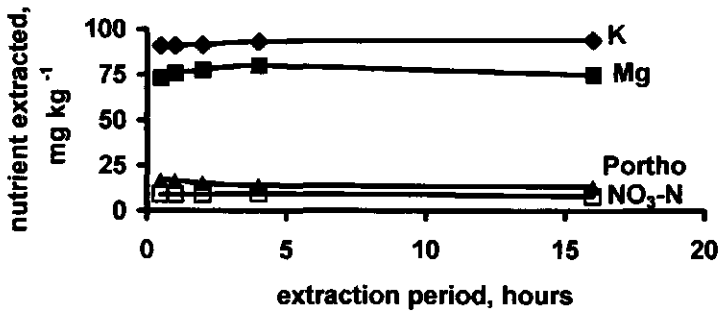

FIGURE 2. Effects of extraction period on the amounts of extractable nitrate (NO_3-N), ortho-phosphate (P_{ortho}), potassium (K) and magnesium (Mg). Unpublished results of a sand soil.

Effect of extraction temperature

Extraction temperature has a clear effect on the amount of extractable P_{ortho} and K [83] and quantity-intensity relationships [13]. Increasing the temperature during extraction increases the amount of nutrient extracted. This effect is the result of the effect of temperature on the rate constant of kinetic processes and on the equilibrium constant of soil chemical processes. Houba [33] found that increasing the extraction temperature from 20°C to 80° C in the 0.01 M $CaCl_2$ procedure has almost no effect on extractable NO_3 but increased the NH_4 and total N by a factor 2 to 3, on average. To diminish temperature effects on nutrient extraction and to compare extraction results, extraction temperature should be standardized. In the 0.01 M $CaCl_2$ procedure the extraction temperature is set at 20°C

Effect of repeated extractions.

In most soil testing programs a soil sample is extracted only one time. However, repeated extractions with $CaCl_2$ solutions show that P_{ortho} [17,49], K [69,85] and Mg [27] are extracted from the soil every cycle. The course of the relation between the total amount of extractable nutrient and number of extractions differ between the nutrients but also for the same nutrient. We found that the 0.01 M $CaCl_2$ procedure

extracts 20 - 50 percent of the total amount of exchangeable K on clay soils and 50-80 percent of the total amount of exchangeable K on sand soils (data not presented). Schachtschabel [70] and Grimme [30] found that 0.0125 M $CaCl_2$ extracted on average 85 percent of exchangeable Mg and 10-60 percent of exchangeable K, respectively.

Chemical conditions during extraction

The ionic composition, ionic strength and pH of the soil solution under field conditions depends on or varies with many factors [3,16,26,29,48,56,61,64,80,94,96]. Mostly, the Ca concentration in the bulk soil solution is between 1 and 10 mM [56], but may vary from less than 0.1 mM Ca in slightly acid soils [64] to almost 100 mM in the rhizosphere [26,96]. Calcium, along with Mg, is the major cation counteracting the anions chloride (Cl), NO_3, SO_4, bicarbonate (HCO_3) and organic anions [64] in the soil solution. The concentrations of these anions range from less than 0.1 mM to more than 200 mM in sodic soils [26]. In general, the Cl concentration is less than 20 mM [26]. The ionic strength of the soil solution may vary from 0.1 to more than 10 mM in the bulk soil solution [16,48]. In the rhizosphere, the ionic strength can be higher than 50 mM [29,94]. The soil solution pH is buffered by many soil chemical processes and may vary from less than 4 to more than 8.

When soils are extracted according to the 0.01 M $CaCl_2$ procedure, the ionic strength and the concentrations of Ca and Cl in the soil suspensions of non-sodic agricultural soils are almost equal to those of the 0.01 M $CaCl_2$ extractant (Figure 3). This can be explained by the wide soil-solution ratio during the 0.01 M $CaCl_2$ procedure. The Ca concentration may deviate from 0.01 M because of precipitation/dissolution of Ca-salts in the soil, cation exchange reactions or changes in the variable charge properties of soil particles [43].

The pH of 0.01 M $CaCl_2$ solution is about 5.7 and 'unbuffered'. During the extraction procedure the pH of the soil suspension changes to the actual soil pH. Schofield [73] advised a 0.01 M $CaCl_2$ soil extraction (1:5 w/v) for the determination of the actual soil pH. Deviations from the advised 1:5 soil-solution ratio have a small, neglible effect on the actual soil pH [11]. From this all it can be concluded that during the 0.01 M $CaCl_2$ procedure the pH of the soil suspension is almost equal to the actual soil pH and the

ionic strength and the concentration of Ca are comparable to the average ionic strength and Ca concentration of the soil solution under field conditions. This may facilitate interpretation and translation of soil testing results to field conditions.

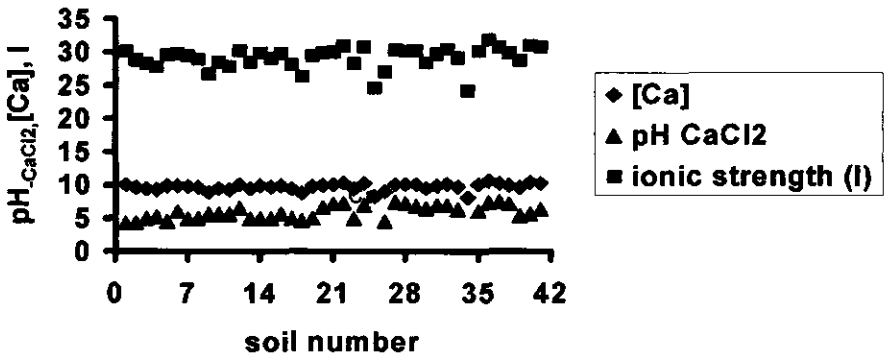

FIGURE 3. The calcium concentration ([Ca]) and ionic strength (I), both in mM l^{-1}, and pH-$CaCl_2$ of the soil suspension of 41 agricultural soils extracted according the 0.01 M $CaCl_2$ procedure. The Ca concentration, ionic strength and pH of the 0.01 M $CaCl_2$ extractant were on average 10 mM, 30 mM and 6, respectively. Unpublished results.

Nutrient intensity and the 'labile' pool of soil nutrients

An extraction procedure is valuable for a soil testing program if the amount of nutrients extracted is related to or equal to the nutrient concentration in the soil solution or the pool of 'labile' plant nutrients in the soil. In literature, the amount of nutrients extracted with 0.01 M $CaCl_2$ is often called 'nutrient intensity' according to the Schofield concept [74]. However, the 'nutrient intensity' reflects the 'strength of retention' by which a nutrient is held in the soil; with other words, the nutrient concentration. However, the nutrient concentration in the soil suspension or the amount of nutrient extracted by 0.01 M $CaCl_2$ is not equal to the 'nutrient intensity': the nutrient concentration in the soil suspension depends on the soil-solution ratio. Only, the pH of the soil suspension is independent of soil-solution ratio and is related to the H^+ intensity. This means that

the suggested equalness between nutrient intensity and the nutrient concentration after a 0.01 M $CaCl_2$ extraction is misleading, except for pH.

Houba [32] found a good relationship between Na, K, Mg and P_{ortho} extracted with conventional extraction methods and the 0.01 M $CaCl_2$ procedure suggesting that the 0.01 M $CaCl_2$ procedure extracts nutrients related to the 'labile' pool of soil nutrients. In literature it is well known that the major part of the 'labile' pool of cations is made up by the cations bound at the exchange complex. Moreover, the cations at the exchange complex determine the nutrient concentration in the soil solution. Our results showed that 0.01 M $CaCl_2$ extracts only part of the exchangeable cations. Repeated extractions increased the amount of $CaCl_2$ extractable nutrients. This shows that during every 0.01 M $CaCl_2$ extraction a 'new' chemical 'equilibrium' is established in the suspension. Kinetically fast reactions, like cation exchange and some precipitation/dissolution processes, determine the equilibrium concentration. These fast processes also determine the nutrient intensity and the size of 'labile' pool of plant available nutrients under field conditions. Further research is necessary to relate the composition, pH and ionic strength of the supernatant to the amount of plant available soil nutrients. Specific knowledge of exchange and dissolution/precipitation processes [10,13,72,73,-74,91] in the soil is necessary for this. Computer models [54] which calculate the distribution of nutrients over the soil-solution system may be a helpful tool.

Laboratory aspects

Multi-nutrient extractants reduce the number of single nutrient soil extractions, the use of various chemicals, and will facilitate optimization and automation of laboratory activities. The 0.01 M $CaCl_2$ procedure is easy to execute, not labour intensive and the use of chemicals is minimized. Moreover, the demands on laboratory equipment and laboratory conditions are restricted.

The ionic strength of the soil suspension and the presence of Ca^{2+} during the 0.01 M $CaCl_2$ extraction procedure promote coagulation of the soil particles and simplify the separation of soil particles and solution during centrifugation. The supernatant is generally perfectly clear, which facilitates the measurement of very faint colours [74]

The use of the 0.01 M $CaCl_2$ procedure for soil testing programs will give more

information on the soil nutrient status compared to conventional single nutrient procedure. Therefore, the costs of soil analyses according a 0.01 M $CaCl_2$ soil testing program will be relatively low compared single nutrient soil testing programs.

Application of $CaCl_2$ solutions as a soil extractant in practice

Thus far, $CaCl_2$ solutions have been used as a soil extractant in many soil extraction procedures [Table 2]. Generally, these procedures focus on the determination of one nutrient and may differ in $CaCl_2$ concentration, soil-solution ratio, shaking time, extraction temperature, etc. These differences obstruct comparison of results.

In plant nutritional and soil chemical research 0.01 M $CaCl_2$ solutions have been used for the determination of the relationship between the soil status of many nutrients and crop response (e.g. Table 2), the assessment of the nitrogen (N) mineralisation capacity of soils [25], the amount of water soluble phosphate [60], the phosphate potential [74] and soil pH [73].

Extraction with 0.01 M $CaCl_2$ has also been used to extract biomass S [19]. Moreover, it has been used as a 'background' electrolyte studying phosphate adsorption/desorption processes [17,24] and nutrient quantity/intensity relationships [15,50,92].This enumeration shows the practicability of 0.01 M $CaCl_2$ soil extraction in soil testing.

Perspectives of a 0.01 M $CaCl_2$ soil testing program

In a soil testing program the amount of nutrient extracted with a soil extractant is grouped in a nutrient status class. For each class a fertilizer application rate is recommended at which an optimal crop yield and/or crop quality can be obtained. These fertilizer application schemes are most times specific for regions, crops or soils. Many long-term pot and field experiments are necessary to develop fertilizer application schemes in soil testing programs. Prerequisite, for a 0.01 M $CaCl_2$ soil testing program is a robust 0.01 M $CaCl_2$ procedure.

Taking into account the effect of soil drying, drying temperature, extraction temperature, soil-solution ratio, extraction time and duration and temperature during storage period [38], standardization of the 0.01 M $CaCl_2$ extraction procedure is necessary

TABLE 2. Listing of pot and field experiments in which $CaCl_2$ solutions have been used as a soil extractant.

Element [1]	Pot-/field-experiment [2]	Crop [3]	Crop respons [4]	r^2 [5]	Remarks [6]	Comparison [7]	Ref. [8]
Al	P	B,R,A	DMA,CA	0.19 - 0.61	D(?)-R(?)-S1-T1-C	Y	41
Al	P	Bu,R	DMA;CA	0.42 - 0.83	D(?)-R(?)-S1-T1-C	Y	43
Al	P	B	DMA	0.49	D-R(?)-S1-T1-C	Y	88
Al	P	Po,Ph	DMP;CP	n.s - 0.58	D-R-S1-T1-C	Y	55
B	P	He	CA	0.87	D-R-S1-T1-C	Y	1
B	P	He	CA,DMA	n.d.	D-R-S1-T1-C	Y	2
B	P/F	Soy,T,A,Ru	UA,CA	0.08 - 0.90	D-R(?)-S1-T1-C	Y	66
Cd	P	T	CA	0.91 - 0.92	D(?)-R1-S1-T1-C	N	89
Cd	P	Le	CA	0.89 - 0.91	D-R(?)-S/S1-T/T1-C/C1	Y	5
Cd	P	Le,Mu	UA	0.79	D(?)-R(?)-S(?)-T(?)-C	Y	87
Cd,Cu,Ni,Zn	F/P	Le,En,Sp,M	CA,DMA	0.65-0.99	D-R-S/S1-T-C	N	59
Cd,Cu,Pb	P	W	UT	n.s. - 0.86	D(?)-R1-S1-T1-C	Y	52

(continued)

TABLE 2. Continued

Element [1]	Pot-/field-experiment [2]	Crop [3]	Crop respons [4]	r^2 [5]	Remarks [6]	Comparison [7]	Ref. [8]
Cu,Zn	P	R	CA,UA	n.s.- 0.94	M(?)-R(?)-S1,T1,C	Y	76
K	P	L	CA,UA	0.47 - 0.92	M-R(?)-S-T1-C	Y	68
K	P	G	UA	0.82	D(?)-R1-S1-T1-C	Y	77
K	P	Ba,So,Co,Pe	UA	0.02-0.64	D/M-R(?),S,-T1-C	Y	85
K	P	Ri	DMA,DMP, UA	0.76-0.86	M-R(?)-S1-T1-C/C1	Y	57
K	P/F	Oa,Be,W	FYP	0.72-0.75	D-R(?)-S-T1-C1	N	31
K	F	Oa	CA	0.27-0.59	D-R-S-T-C1	Y	71
K	F	Cot	CP,DMP	0.49- 0.69	D-R(?)-S-T1-C	Y	18
K,P_{ortho}	P	G	DMA;UA	0.27 - 0.55	D-R(?)-S-T-C	Y	82
K,P_{ortho},Mg	P	B,M	DMA;UA	0.55 - 0.85	D-R(?)-S-T--C	Y	22
Mg	P	G,Br	UA	0.62- 0.80	D-R(?)-S1-T1-C	Y	28
Mg	P	R	UA,CA	0.02 -0.02	D(?)-R(?)-S-T1-C1	Y	62
Mg	P	G	UA	0.88	D(?)-R(?)-S-T-C1	Y	75

(continued)

TABLE 2. Continued

Element [1]	Pot-/field-experiment [2]	Crop [3]	Crop respons [4]	r^2 [5]	Remarks [6]	Comparison [7]	Ref. [8]
Mn	P	R,Bu	CA	0.70 - 0.76	D(?)-R(?)-S1-T1-C	Y	43
Mn	P	B,R,A	CA	0.31- 0.76	D(?)-R(?)-S1-T1-C	Y	42
Mn	F	Ap	CP	0.12 - 0.29	D(?)-R-S1-T1-C1	Y	58
Mn	P	T,G	UA,CA,DMA,UP, CP,DMP	n.s- 0.66	M-R(?)-S1-T2-C/C1	Y	93
NO_3, NH_4, N-org, Ntot	P	G	UA,DMA	0.29 - 0.87	D-R-S-T-C	Y	6
NO_3, NH_4, N-org, Ntot	P	G	UA	n.s.- 0.63	D-R-S-T-C	Y	89
NO_3,NH_4, Norg	F	Sb	UA,UP	0.16 -0.68	D-R-S-T-C	Y	35
N,S	P	Ca	UA	0.57-0.96	D(?)-R(?)-S1-T1-C1	Y	63
P_{ortho}	P/F	B;G;W	UA;	0.6 - 0.9	D/M-R(?)-S/S1-T-C	Y	44,45
P_{ortho}	P	G	DMA;UA	0.25 - 0.50	D(?)-R(?)-S1-T1-C	Y	81
P_{ortho}	P	B	DMA;CA;UA	0.07 - 0.38	D(?)-R(?)-S1-T1-C	Y	84
P_{ortho}	P	G	CA,UA	0.56-0.77	?-?-?-?-C	Y	8

(continued)

TABLE 2. Continued.

Element [1]	Pot-/field-experiment [2]	Crop [3]	Crop respons [4]	r^2 [5]	Remarks [6]	Comparison [7]	Ref. [8]
P_{ortho}	P	G	CA,UA	0.43-0.46	?-?-?-?-C	Y	20
S	P	A	DMA	0.69	D-R(?)-S1-T1-C	Y	86
S	P	G	UA,DMA	0.62- 0.77	D(?)-R(?)-S1-T1-C	Y	95
S	P	Soy	UA,DMA	0.57-0.96	D-R(?)-S(?)-T(?)-C1	Y	78
Zn	P	M,Oa	UA	0.27-0.29	D-R(?)-S1-?-C	Y	51
Zn	F	Pe	CP	0.86	D-R(?)-s1-t1-C/C1	Y	21

(continued)

TABLE 2 continued

[1] Element under study.
[2] Field-/pot experiments: field (F) or pot (P) experiment or both (F/P),
[3] Crop: A=alfalfa; Ap=apple; B=barley; Ba=blackgram; Be=bean; Br=brassica; Bu=buckwheat; Ca=Canola; Cl=clover; Co=cowpea; Cot=cotton; En=endive; G=grass; He=helianthus; L=lotus; Le=lettuce; M=maize; Mu=mustard; Oa=oats; Pe=pearl millet; Pea=peanut; Ph=Phaseolus; Po=Poa; R=rape(seed); Ri=rice; Ru=rutabago; So=sorghum; Soy=soybean; Sp=spinach; Sb=Sugar beet; T=Trifolium; W=wheat
[4] Crop respons
UT,UA,UP = uptake total plant (UT), uptake aboveground part (UA), uptake in plant part (UP) or combinations (UT/UA/UP)
CT,CA,CP = concentration total plant (CT), concentration aboveground part (CA), concentration plant part (CP) or combinations (CT/CA/CP)
DMT,DMA,DMP= dry matter total plant (DMT), dry matter aboveground part (DMA), dry matter plant part (DMP) or combinations (DMT/DMA/DMP)
FYT,FYA,FYP= fresh yield total plant (FYT), fresh yield aboveground part (FYA), fresh yield plant part (FYP) or combinations (FYT/FYA/FYP)
[5] Explained variance of the relationship of the amount of nutrient extracted by 0.01 M $CaCl_2$ and crop response.
[6] Remarks:
(?) = *not mentioned or described in article*
D,M = dry (D) or moist (M) soil sample or both (D/M)
R,R1 = room (R) temperature, others (R1) or both (R/R1)
S,S1 = shaking ratio 1:10 (w/v) (S) or others (S1) or both (S/S1)
T,T1 = shaking time 2 hours (T), others (T1) or both (T/T1)
C,C1 = 0.01 M $CaCl_2$ (C), others (C1) or both (C/C1)
[7] Comparison = comparison with other soil extractant (Y=yes; N=no)
[8] Literature references

At this moment the pretreatment of soil samples [46] and determination of nitrogen fractions [47] are standardized internationally. The 0.01 M $CaCl_2$ extraction procedure is already part of soil exchanges programs like WEPAL [37] and certified soil reference material is available [40]. The coefficient of variation of the repeatability for pH, NO_3, NH_4, N, P_{ortho}, Na, K and Mg varied from 0.47 percent for pH to 5.8 percent for N. The coefficient of variation for the reproducibility varied from 1.26 percent for pH to 18.72 percent for NH_4-N [40].

The setup of a multi-nutrient 0.01 M $CaCl_2$ soil testing program, including definition of nutrient status classes and fertilization schemes, is time consuming and expensive. The applicability of the literature data (Table 2) is restricted because the procedures differ widely. Moreover, the test crops and the crop responses determined differ widely. Despite this, Table 2 shows that the amount of nutrients extracted by 0.01 M $CaCl_2$ may explain a considerable part of the variance in crop response. Houba [32] found a good relationship between Na, K, Mg and P_{ortho} extracted with conventional extraction procedures and the 0.01 M $CaCl_2$ procedure. Houba proposed to carry out calibration studies between conventional procedures and 0.01 M $CaCl_2$ procedure and to convert the nutrient status classes and fertilizer recommendation schemes of conventional soil testing programs into 0.01 M $CaCl_2$ nutrient status classes and fertilizer recommendation schemes. Subsequently, these 0.01 M $CaCl_2$ soil testing programs should be tested in pot and field trials. A detailed calibration of conventional procedures and the 0.01 M $CaCl_2$ extraction procedure for pH, Mg and K has been carried out by Fotyma et al. [23], Loch et al. [53] and Baier et al. [9], respectively.

Nowadays, agricultural farms are confronted with an increasing amount of agricultural, environmental and legislative constraints and boundary conditions. This will necessitate farmers to manage the nutrient flows on their farms more and more. Helpful tools are soil and plant analyses to control or diagnose soil nutrient status, and computer models to calculate the need for additional nutrient application. The 0.01 M $CaCl_2$ procedure as a part of a multi-nutrient 0.01 M $CaCl_2$ soil testing program and the expected relationship between the amount of nutrients extracted and the size of the

'labile' pool of soil nutrients, makes the 0.01 M $CaCl_2$ procedure a valuable tool in future farm nutrient management.

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CHAPTER 4

EFFECT OF DRYING TEMPERATURE ON AMOUNT OF NUTRIENT ELEMENTS EXTRACTED WITH 0.01 M $CaCl_2$ SOIL EXTRACTION PROCEDURE

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EFFECT OF DRYING TEMPERATURE ON AMOUNT OF NUTRIENT ELEMENTS EXTRACTED WITH 0.01 *M* $CaCl_2$ SOIL EXTRACTION PROCEDURE

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ABSTRACT

In the current soil drying protocol of the 0.01 *M* calcium chloride ($CaCl_2$) procedure, soils are oven dried at 40°C for 24 h. At this drying temperature, as well as at lower drying temperatures, a change of the actual soil nutrient element status cannot be excluded because microbes will be active during part of the drying period. However, a higher drying temperature may affect soil characteristics and soil processes and also lead to a misinterpretation of the soil nutrient element status. An explanatory study was conducted to get more insight into the effect of i) oven drying temperature and ii) the use of forced-air ventilation at low drying temperatures on nutrient elements extracted with the 0.01 *M* $CaCl_2$ procedure. The goal of the study was to investigate the perspectives of optimiza-

tion of the soil drying protocol of the 0.01 *M* $CaCl_2$ procedure. Three moist test soils with different soil characteristics were oven dried at 20 and 40°C with and without forced air ventilation and at 70 and 105°C without forced-air ventilation. The moist test soils and the dried soils were extracted with a 0.01 *M* $CaCl_2$ solution and pH and total N (N), ammonium-nitrogen (NH_4-N), nitrate-nitrogen (NO_3-N), *ortho*-phosphate (*ortho*-P), potassium (K), magnesium (Mg), sodium (Na), and manganese (Mn) determined in the supernatant after centrifugation. Soluble organic N (org-N) was calculated as the difference between N and the summation of NH_4-N and NO_3-N. In the temperature range from 40 to 105°C, *ortho*-P, NH_4-N, org-N, and Mn extracted tended to increase two or threefold for each 30–35°C increase in drying temperature. Differences in *ortho*-P, NH_4-N, org-N, and Mn extracted at 20 and 40°C were relatively small. The pH, K, Na, and NO_3-N extracted were affected by drying temperature but the effect was variable. Magnesium extracted was not affected by drying temperature. The use of forced air ventilation at 20 and 40°C had no significant effect on the amount of org-N, NH_4-N, *ortho*-P, K, and Mg extracted. There were significant effects of forced-air ventilation on pH and NO_3-N, Na, and Mn extracted but the effects were variable. Test values (60–70%) of the moist test soils were significantly different from the respective test values of the test soils dried at 20 and 40°C with and without forced-air ventilation. Based on the differences between moist and dried soils, it is questionable if soil drying should be recommended in the 0.01 *M* $CaCl_2$ procedure. Therefore, further research should focus on the relationship between soil test values of moist and dried soils with crop response. If soil drying is preferable drying temperature should not exceed 40°C.

INTRODUCTION

Soil testing programs are a practical tool for farmers to optimize their fertilizer application rates. In soil testing programs, fertilizer recommendations are based on the actual soil nutrient element status and crop demand. The power of a soil testing program is, therefore, mainly determined by its ability to determine the field nutrient element status adequately. To achieve this i) soil sampling techniques in soil testing programs have been improved to cope with soil variability, ii) soil samples are dried as soon as possible after sampling to stop microbial processes, which may alter the soil nutrient element status, during transportation and storage, and iii) laboratory protocols have been developed and improved to

ensure precise, accurate, and reproducible soil test values. To optimize laboratory activities and to minimize costs, laboratories strive for a reduction in the drying period. Oven drying at high temperatures, if necessary combined with forced air ventilation, are common methods to achieve this. During the oven drying process, the water content of the soil sample decreases, the air content increases, and the soil temperature will reach the oven temperature.

At low soil water content, soil microbial activity may be reduced (1). Microbes differ in their tolerance level for low soil water potentials. Nitrifiers like *Nitrosomonas* spp. have a tolerance level of −1.5 MPa whereas ammonifiers like *Clostridium* spp. and *Penicillium* spp. have a tolerance level of −10−−25 MPa, respectively (1). This may explain the commonly observed NH_4-N accumulation during soil drying (2,3). When the water potential becomes very low, microbes will succumb because of desiccation (2). The soil extraction solution may then contain hydrolyzable compounds originating from soil microbial biomass, such as proteins and aminosugars (4).

Lowering the soil water content also leads to an increase of the concentration of solutes and thus the ionic strength of the remaining solution. This may lead to precipitation and (specific) adsorption/desorption processes in the soil and to changes in the magnitude of the charge of variable charge sites (5). The increase in air content affects oxidation–reduction processes related to, e.g., organic matter, iron (Fe), and Mn (5). All these soil chemical processes occur simultaneously during soil drying and will affect the partitioning of chemical species between the liquid and solid phase. After rewetting a dried soil, the composition of the newly established soil solution differs from that of the original moist soil (6,7). The irreversibility of many of the above soil processes are probably responsible for this phenomenon (5). During the drying process, water is also extracted from soil organic matter causing disconnection of hydrogen bonds and contraction of organic matter structures (8). Guggenberger et al. (9) theorized that soil organic matter has other disaggregation and/or stretching characteristics after contraction compared with the original soil organic matter. Therefore, rewetting a dry soil will result in fragmentation of the contracted organic matter with consequent increase of soluble organic carbon (10). Oven temperatures between 25 and 35°C coincide with the temperature range of maximal microbial activity (1). Therefore, microbial activity cannot be excluded during (part of) the drying process when the drying temperature is in this range. At drying temperatures higher than 40°C soil microbial activity decreases drastically and most soil microbes die off because of the thermal denaturation of proteins and alterations in the permeability of membranes (2). Raised temperatures also increase reaction rates of soil chemical reactions (5). From the above considerations it will be clear that soil drying may seriously affect soil characteristics and processes and therefore could change the actual soil nutrient status. Several studies confirm this (11–14). Houba et al. (15) have proposed 0.01 *M* $CaCl_2$ as a multinutrient soil extractant. The perspectives of the 0.01 *M*

$CaCl_2$ extraction procedure for the development of a multinutrient soil testing program are promising (16). However, the standardized $CaCl_2$ extraction procedure extracts a soil sample that is dried at 40°C for 24 h (17). This drying temperature may result in a relatively long drying period and changes of the soil status because of microbial activity. On the other hand at this drying temperature, soil characteristics and processes may already be affected and change soil test values. Optimization of the drying protocol is, therefore, desirable. An explanatory study has been carried out to get more insight into the effect of i) oven drying temperature and ii) forced-air ventilation at low drying temperatures on pH and N, soluble organic N (org-N), NH_4-N, NO_3-N, *ortho*-P, K, Mg, Na, and Mn determined via the 0.01 *M* $CaCl_2$ extraction procedure. Goal is to study the perspectives of optimization of the drying protocol of the $CaCl_2$ procedure.

MATERIALS AND METHODS

The impact of the soil drying protocol in the 0.01 *M* $CaCl_2$ procedure on soil test values may depend on soil characteristics. Therefore, three test soils were selected differing in their content of organic matter, clay, and carbonate as well as in their cation exchange capacity (CEC) (Table 1). The samples were taken from the top layer (0–30 cm) of arable soils. After collection in the field, each of the test soils was immediately sieved through a 5-mm sieve and then split up into two parts. One part, the moist soil sample, was extracted immediately according the 0.01 *M* $CaCl_2$ procedure (17). The water content of the moist soil was determined after drying a subsample at 105°C for 24 h. The other part was split into six lots. All lots were spread out in a shallow layer of 1–2 cm on trays covered with water resistant paper and mixed at regular time intervals during a 24 h drying period. Four lots were dried at 20°C, 40°C, 70°C, and 105°C, respectively, without forced-air ventilation. These lots were characterized as 20C, 40C, 70C, and 105C, respectively, and used to study the effect of oven drying temperature. Two lots

Table 1. Characteristics of the Test Soils

	Characteristic			
Soil	Organic Matter (%)	Clay (%)	$CaCO_3$ (%)	CEC, cmol (-) kg^{-1}
Calcareous clay soil	8.7	26	10	18
Sandy soil	3.5	4	0	6.5
Noncalcareous clay soil	16.5	28	0	29

were dried at 20°C and 40°C, respectively, with forced-air ventilation and characterized as $20C^+$ and $40C^+$. These two treatments together with the 20C and 40C treatments were used to study the effect of forced-air ventilation at low temperatures. The perspectives of optimization of the drying protocol were evaluated by comparing soil test values of the moist treatment with the 20C, $20C^+$, 40C, and $40C^+$ treatments. After drying, the six lots were crushed gently and passed through a 2-mm sieve and stored in plastic bottles with screw caps. The dried soil samples were then extracted according to the 0.01 *M* $CaCl_2$ procedure (17). To limit storage effects on pH and extractable nutrient elements (11,18,19) the soil samples were extracted as soon as possible after drying. The water content of the dried soil samples just before extraction was determined by drying a representative subsample at 105°C for 24 h. After 2 h extraction time, pH was measured in the settling suspension. The concentrations of Mg, K, Na, N, NH_4-N, NO_3-N, and *ortho*-P were determined in the clear centrifugate of the soil suspension. Sodium and K were determined by flame emission spectrometry, Mg and Mn by atomic absorption spectrometry, and *ortho*-P, NO_3-N, NH_4-N, and N spectrophotometrically by means of a segmented flow technique (17). When the P concentrations were very low, 4-cm cuvettes instead of 1-cm cuvettes were used. The experiment was carried out in fivefold. Org-N, the amount of soluble organic N, was calculated as the difference between (total) N extracted and the summation of extracted NO_3-N and NH_4-N. The results were expressed as the amount of nutrient elements extracted in mg kg^{-1} dry soil (dried at 105°C).

The reproducibility of the analytical results was determined by the coefficient of variation (CV) = [standard deviation × 100%]/[mean of the replicates].

The experimental results were statistically analyzed using analysis of variance. When the analysis of variance showed significant effects ($P = <0.05$), differences between the treatments were tested by the Tukey test ($P = <0.05$). The statistical analysis were carried out with the statistical package Genstat 5 (20).

RESULTS AND DISCUSSION

Statistical Analysis

The CV of the analytical results are given in Table 2. Four CV classes have been considered: <10, 10–15, 15–20, and >20%. Coefficient of variation values in the <10, 10–15, 15–20, and >20% classes are assumed to be good, moderate, bad, and unacceptable, respectively. The reproducibility of the analytical results were good for pH, N, NO_3-N, Na, K, and Mg. A large number of observations for *ortho*-P, NH_4-N, and Mn occurred in the CV classes 15–20% and >20% and resulted from (very) low absolute values of the mean. The low absolute values

Table 2. Calculated CV of the Experimental Results of pH and Nutrients Extracted from the Test Soils According the 0.01 *M* $CaCl_2$ Procedure[a]

	CV (%)			
Parameter	<10	10–15	15–20	>20
pH	21	0	0	0
N	18	2	1	0
NH_4	17	1	0	3
NO_3	16	4	1	0
ortho-P	8	2	2	9
Na	21	0	0	0
K	20	1	0	0
Mg	21	0	0	0
Mn	15	1	0	5

[a]CV is tabulated in classes and the total number of observations per parameter is 21.

were found in the moist soil samples (NH_4-N, Mn, and *ortho*-P) and in the clay soils (*ortho*-P). The CV results agree with certification work of a soil sample for pH and nutrients extracted by 0.01 *M* $CaCl_2$ (21). It is concluded that these experimental results could be used for further study.

Water Content

The soil samples were taken during a rainy period. As a result water content was (very) high: 11.3, 76.3, and 27.21%(w) for the moist sand soil and moist calcareous and moist noncalcareous clay soils, respectively (Fig. 1). Just before extraction, i.e., after drying and storage, water content of the 105°C treatment sand soil, noncalcareous clay, and calcareous clay soils was 0.6, 3.8, and 4.9% again. This shows that during sieving, storage, or weighing out the soils have adsorbed water. Water content of the dried soils just before extraction was markedly lower than water content of the field moist test soils. In the clay soils water content decreased as drying temperature increased. Water content of all drying treatments of the sand soil was about 1% and always lower than the water content of the same treatments of the clay soils. The use of forced-air ventilation at 20 and 40°C lowered the water content of the clay soils with 0.9–5.7%, but had no clear effect on water content of the sand soil. Since dried soils seem to adsorb water after the drying process, soil water content should always be determined prior to extraction to avoid misinterpretations of 0.01 *M* $CaCl_2$ soil test results.

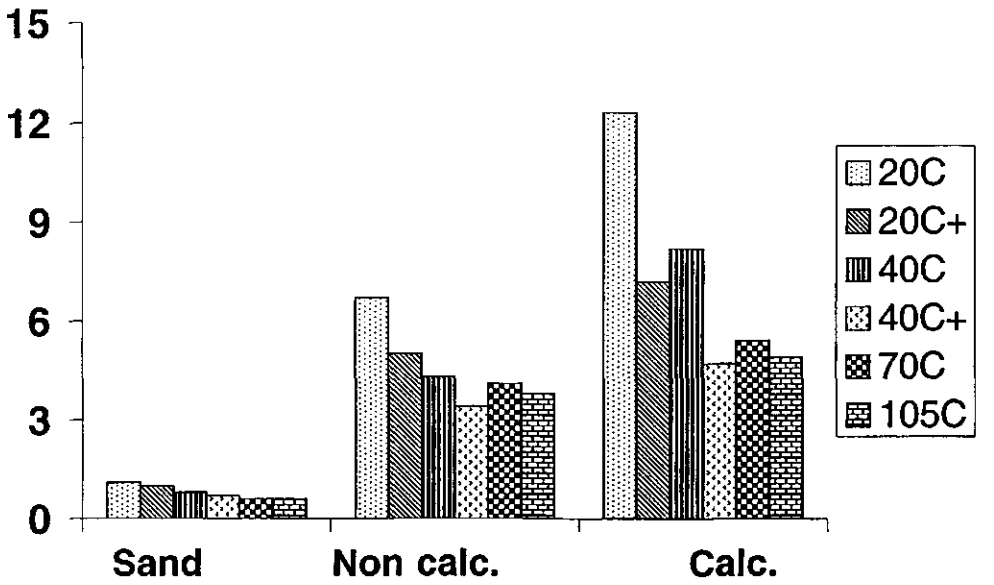

Figure 1. Water content of the soil samples after drying and just before extraction, in percentage. Drying treatments: 20C, 40C, 70C, and 105C are the soils dried without forced-air ventilation at 20°C, 40°C, 70°C, and 105°C, respectively, and $20C^+$ and $40C^+$ are the soils dried at 20°C and 40°C with forced-air ventilation. Sand: sand soil, Calc.: calcareous clay soil, and Noncalc.: noncalcareous clay soil.

General

The results for pH, Mg, K, Na, and NO_3-N showed a normal distribution, thus allowing straight forward statistical analysis. The experimental results of Mn, org-N, NH_4-N, and *ortho*-P had to be transformed to a log-normal distribution prior to statistical analysis.

Table 3 gives an overview of the experimental results. Differences in pH and extracted nutrient elements between the treatments result from differences in the course of water content and soil temperature of the test soils as a function of time.

pH

After drying at 105°C, the pH of the test soils was always significantly lower than after drying at 70°C. The pH lowering was maximal, i.e., 0.2 pH unit, in the noncalcareous clay soil, which had the highest organic matter content. In the sand soil as well as in the noncalcareous clay, soil pH was not significantly different between the 20°C and 40°C treatments. Soil pH in the calcareous clay soil dried according the 40°C treatment was significantly higher than pH of the same soil

Table 3. The pH, Mn, org-N, NH_4-N, NO_3-N, *ortho*-P, Na, K, and Mg Extracted According the 0.01 *M* $CaCl_2$ Procedure[a]

	Sand				Noncalcareous				Calcareous			
	20C	40C	70C	105C	20C	40C	70C	105C	20C	40C	70C	105C
pH	6.08a	6.13a	6.19b	6.09a	6.31a	6.30a	6.24b	6.04c	6.89ab	6.96c	6.94bc	6.88a
Mn	0.67a	1.25b	4.14c	14.4d	0.55a	0.97a	3.89b	12.8c	0.18a	3.94b	12.3c	36.0d
org-N	2.78a	2.80a	5.31b	13.3c	6.21a	7.50a	20.2b	38.2c	16.3a	18.1a	37.9b	114.9c
NH_4-N	1.37a	2.32ab	2.25ab	5.94b	1.71a	2.41ab	3.42ab	7.38b	5.96a	7.93a	10.9a	23.2b
NO_3-N	6.14a	6.19a	6.30a	6.18a	3.57a	5.32b	1.28c	1.82c	0.84a	8.88b	3.92c	5.55d
ortho-P	2.61a	3.25ab	4.32ab	5.60b	0.05a	0.06a	0.29b	0.85c	0.17a	0.22ab	0.34bc	0.50c
Na	16.3a	15.8a	15a	14.1a	36.4a	33.0b	32.1b	33.2b	48.9a	45.4b	41.8c	42.0c
K	126.25a	130a	124a	113b	122.6a	111b	98.1c	108b	51.8a	54.7a	52.1a	52.5a
Mg	48.6a	51.3a	49.0a	44.9a	218a	199a	211a	208a	205a	206a	202a	203a

[a] 20C, 40C, 70C and 105C are the drying treatments at 20°C, 40°C, 70°C, and 105°C, respectively. Nutrients are expressed in mg kg^{-1} dry soil. For each soil the test results of the treatments are not significantly different ($P = 0.05$) when followed by the same letter.

dried according the 20°C treatment. An increase of drying temperature from 40°C to 70°C resulted in a significant pH increase in the sand soil, a significant pH decrease in the noncalcareous clay soil, and had no significant effect on pH in the calcareous soil. A pH lowering because of soil drying is generally attributed to the production of H_3O^+ because of hydrolysis or oxidation of organic compounds or from the exposure of acidic groups to the solution due to fragmentation of soil organic matter (10). There is no explanation for a pH increase because of drying. According to ISO 10390 (22) the acceptable variation (repeatability) of pH measurements of soils in the pH range smaller than 7.0 equals 0.15 pH units. Therefore, pH values in soil testing programs as well as pH values in most liming recommendation schemes are generally expressed in one decimal. Thus, most of the significant effects found in our experiment are small and negligible from a practical point of view.

Manganese

In all test soils extracted Mn increased significantly when drying temperature increased. The difference in extracted Mn between the 20°C and 105°C treatment was maximal on the calcareous clay soil. Increasing drying temperature from 40 to 70°C and from 70 to 105°C yielded on average three-fold amount of extracted Mn from each of the test soils. An increase of extracted Mn has often been reported for several soil extractants (11,12,23,24) and is generally attributed to the release of organically bound Mn and the reduction of insoluble Mn^{4+} compounds.

Organic-Nitrogen

Org-N extracted by 0.01 *M* $CaCl_2$ may be an important indicator of the soil N status because it is thought to be related to the soil mineralization potential (25). In each test soil org-N extracted was not significantly different between the 20°C and 40°C treatments. When drying temperature increased from 40 to 70°C and 70 to 105°C org-N extracted increased significantly. Increasing drying temperatures from 40 to 70°C and 70 to 105°C yielded on average two or threefold amount of org-N from each of the test soils. Barekzai and Mühling (3) who tested 17 different soils found a six-fold increase in org-N extracted when drying temperature was raised from 40 to 105°C which agrees with our findings. Org-N originates from soil organic matter, crop residues (26), and residues of (dead) soil microbes (4). Water loss rate during the drying process at 70 and 105°C will be very high and associated with a very low microbial activity. The contribution of microbial residues to org-N extracted at 70 and 105°C will, thus, be low and, consequently, org-N originates mainly from soil organic matter. Microbial activity cannot be

neglected during (part of) the drying process at 20 or 40°C because water content of the moist clay soils was relatively high.

Ammonium-Nitrogen

On all test soils extracted NH_4-N showed a tendency to increase when drying temperature increased. The increase in extracted NH_4-N was significant between the 70°C and 105°C treatment. Differences in extracted NH_4-N were not significant between the other treatments. Barekzai and Mühling (3) found that NH_4-N extracted increased by 80%, on average, when drying temperature increased from 40 to 105°C. However, in most of their 17 test soils NH_4-N extracted increased two or threefold, which is in accordance with our present findings. The increase in NH_4-N extracted when drying temperature increased from 70 to 105°C cannot be attributed to microbial activity because there is no ammonification in this temperature range. It is possible that the NH_4 determination by the indophenol blue method was affected by the easily hydrolyzable org-N (27) which was also increased significantly between these treatments or that amino acids present in the extract were measured as NH_4-N (28). We found that up to 20% of org-N could be amino acids (data not presented).

Nitrate-Nitrogen

The amount of extracted NO_3-N from the sand soil was not significantly affected by drying temperature. Probably, drying temperature was too high or water content too low for microbial activity. Drying temperature had an effect on extracted NO_3-N from the clay soils. Extracted NO_3-N from the 20°C treatment was significantly lower than extracted NO_3-N from the 40°C treatment. A lower amount of extracted NO_3-N at 20°C can be attributed to microbial activity, which may lead to the immobilization of NO_3-N because of population growth or to the loss of NO_3-N because of denitrification. Since water content of the moist clay soils was relatively high denitrification losses cannot be neglected during part of the drying period. Extracted NO_3-N from the clay soils dried at 70 and 105°C was always significantly lower than after drying at 40°C. Repetition of this part of the experiment confirmed this NO_3-N loss. Barekzai and Mühling (3) found a comparable decrease in NO_3-N extracted by the 0.01 $CaCl_2$ procedure when drying temperature was raised from 40 to 105°C. There are three possible reasons for NO_3-N losses at higher temperatures. Firstly, a loss because of microbial denitrification is possible, but this is unlikely at high temperatures (29,30). Secondly, the combined presence of NO_3-N, NH_4-N, and soluble organic compounds makes a NO_3-N loss via chemodenitrification possible (30). Thirdly, NO_3-N is bound to

aromatic rings present in the soluble organic material via nitration reactions (30). It is remarkable that the NO_3-N loss at higher temperature did not occur on the sand soil. As long as the problem of NO_3-N losses at higher temperatures is not solved drying temperature should not exceed 40°C.

Ortho-Phosphorus

The amount of extracted *ortho*-P tended to increase when drying temperature increased. Differences in extracted *ortho*-P were not significantly different between the 20°C and 40°C treatments. *Ortho*-P extracted from the test soils dried at 105°C was significantly higher than *ortho*-P extracted at 20°C. This also accounts for the clay soils dried according the 70°C treatment. An increase in extractable *ortho*-P upon drying has been attributed to oxidation of organic matter and the subsequent reduction of Fe^{3+}, releasing previously nonextractable organic and Fe-phosphates (24).

Sodium

Extracted Na tended to decrease when drying temperature increased. However, differences in extracted Na were not significant between the drying treatments of the sand soil. Sodium extracted from the 20°C treatment of the clay soils was always significantly higher than extracted Na from the 40°C, 70°C, and 105°C treatments. This effect may be related to microbial activity since conditions for microbial activity may have been optimal during part of the drying process of the relatively wet clay soils. Differences in extracted Na between the 70°C and 105°C treatment were not significant. The tendency for a lower amount of extracted Na when drying temperature increased suggests that part of the Na is converted into insoluble forms or that the size of the cation adsorption complex has increased.

Potassium

Drying temperature had no effect on the amount of extracted K from the calcareous clay soil. On the sand soil and non-calcareous clay soil extracted K from the 20°C treatment was significantly lower than extracted K from the 105°C treatment. The effect of a 40 and 70°C drying temperature on extracted K is variable. The varying results may be explained by the phenomena found by Rich (31) that soils initially high in K would fix K on drying and that soils initially low in K released "fixed" K on drying.

Magnesium

Drying temperature had no effect on the amount of extracted Mg on all test soils. It suggests that drying temperature has no effect on the soil processes that determine extracted Mg.

Effect of Forced-Air Ventilation

Forced-air ventilation will increase water loss rate and as a result may limit the time period of microbial activity. However, it may promote soil reactions like precipitation and oxidation reactions.

Table 4 gives an overview of the effect of forced air ventilation at 20 and 40°C on pH and extracted nutrients by the 0.01 *M* $CaCl_2$ procedure. At 20 and 40°C the use of forced-air ventilation had no effect on the amount of org-N, NH_4-N, *ortho*-P, K, and Mg extracted from the test soils. The effect on pH and other nutrient elements were variable and difficult to interpret, e.g., in the calcareous clay soil forced-air ventilation resulted at 20°C in a significant increase of extracted Mn but at 40°C it resulted in a significant decrease. Moreover, forced-air ventilation resulted in a significant increase in extracted NO_3-N at 40°C in the sand soil and calcareous clay soil but in a significant decrease in the non-calcareous soil. In general, the results suggest that the effect of forced-air ventilation on

Table 4. Effect of Forced Air Ventilation at a Drying Temperature of 20°C and 40°C on pH and Extracted Nutrients from a Sand Soil, a Noncalcareous Clay Soil, and a Calcareous Clay Soil According the 0.01 M $CaCl_2$ Procedure

	Sand		Noncalcareous		Calcareous	
	20C	40C	20C	40C	20C	40C
pH		+	−		+	
Mn			+		+	−
org-N						
NH_4-N						
NO_3-N		+		−	+	+
ortho-P						
Na			−		−	
K						
Mg						

The + and − means that forced air ventilation resulted in a significant increase or decrease, respectively ($P = 0.05$). Empty cell means there is no significant effect.

Table 5. The pH, Mn, org-N, NH_4-N, and NO_3-N Extracted According the 0.01 *M* $CaCl_2$ Procedure from the Moist Test Soils (Moist) and the Same Soils Dried at 20°C and 40°C without and with (+) Forced Air Ventilation

		Treatment				
	Soil	Moist	20C	20C+	40C	40C+
pH	Calc.clay	6.94	6.89*	6.95	6.96	6.97
	Sand	6.61	6.08*	6.07*	6.13*	6.19*
	Noncalc. clay	6.45	6.31*	6.25*	6.30*	6.33*
Mn	Calc.clay	0.00	0.18*	0.72*	3.94*	2.35*
	Sand	0.09	0.67*	0.82*	1.25*	1.24*
	Noncalc. clay	1.10	0.55*	1.18	0.97	1.07
org-N	Calc.clay	5.70	16.3*	18.9*	18.1*	18.5*
	Sand	1.80	2.78*	2.40	2.80*	2.20
	Noncalc. clay	2.19	6.21*	7.64*	7.50*	8.77*
NH_4-N	Calc.clay	0.07	5.96*	4.84*	7.93*	3.65*
	Sand	0.00	1.37*	1.39*	2.32*	1.69*
	Noncalc. clay	1.78	1.71	2.53	2.41	2.40
NO_3-N	Calc.clay	8.60	0.84*	4.70*	8.88	9.47*
	Sand	5.83	6.14	6.44*	6.19	6.74*
	Noncalc. clay	4.55	3.57*	3.48*	5.32*	3.62*
ortho-P	Calc.clay	0.16	0.17	0.16	0.22	0.26
	Sand	2.60	2.61	2.73	3.25	3.88
	Noncalc. clay	0.13	0.05 *	0.08	0.06*	0.08
Na	Calc.clay	41.2	48.9*	42.5	45.4*	43.9*
	Sand	15.2	16.3	16.1	15.8	15.3
	Noncalc. clay	34.5	36.4	31.3*	33.0	30.7*
K	Calc.clay	45.5	51.8	51.2	54.7*	48.9
	Sand	109.7	126.25*	135*	130*	127*
	Noncalc. clay	167.92	122.6*	128*	11*	105*
Mg	Calc.clay	237	205*	190*	206*	190*
	Sand	47.8	48.6	49.9	51.3	50.5
	Noncalc. clay	238	218	211*	199*	202*

Nutrients are expressed in mg kg^{-1} dry soil. Test values followed by * means that this value is significantly different from the test value of the respective moist soil ($P = 0.05$).

pH and extracted nutrient elements is limited. Probably, the drying period of 24 h outweighed the possible effects of forced-air ventilation.

EVALUATION

The value of a 0.01 *M* $CaCl_2$ soil testing program is determined by its ability to characterize the actual soil nutrient element status at sampling time and on the

relationship between the actual status and crop response. Since it is almost impossible to measure the actual nutrient element status of the soil *in situ*, we assumed that pH and nutrient elements extracted from a moist test soil immediately after sampling at 20°C is the best indicator of the actual soil nutrient element status at the time of sampling. Table 5 gives a summary of the results of a comparative study between the test results of the moist soils and the respective soils given 20C, 20C$^+$, 40C, and 40C$^+$ treatments. In total, 27 comparisons were made per treatment (nine soil test parameters × three test soils). Soils dried according the 20°C treatment gave in 18 out of 27 comparisons a test value which was significantly different from the test value of the respective moist soil. For the 20°C+, 40°C, and 40°C$^+$ this was 16 out of 27, 17 out of 27, and 17 out of 27, respectively. There is no indication that results differed between the test soils. Differences between the moist soils and dried soil cannot be explained by the sieve size used for sieving the moist soil. Shortly after starting the 2 h shaking period, all large soil particles had disappeared. Because of the differences in soil test values of moist and dried test soils it is questionable if the use of dried soils should be recommended in the 0.01 *M* $CaCl_2$ procedure. A decision about this should be deduced from the relationship between soil test values of moist and dried soils extracted with 0.01 *M* $CaCl_2$ and crop response. Until that moment it is recommended to use the current standardized drying protocol.

CONCLUSIONS

The current soil drying protocol of the 0.01 *M* $CaCl_2$ procedure may seriously affect pH and amount of nutrient elements extracted, especially at high drying temperatures. If soil drying is preferable drying temperature should not exceed 40°C.

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CHAPTER 5

RELATIONSHIP BETWEEN MAGNESIUM EXTRACTED BY 0.01 M $CaCl_2$ EXTRACTION PROCEDURE AND CONVENTIONAL PROCEDURES

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RELATIONSHIP BETWEEN MAGNESIUM EXTRACTED BY 0.01 *M* CALCIUM CHLORIDE EXTRACTION PROCEDURE AND CONVENTIONAL PROCEDURES

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ABSTRACT

A multinutrient soil extraction procedure in routine soil testing is attractive. Therefore, it has been suggested to convert conventional soil testing programs into a 0.01 *M* calcium chloride ($CaCl_2$) multinutrient soil testing program using the relationship between test values of the 0.01 *M* $CaCl_2$ extractant and those of the various conventional extractants. However, these relationships are often weak and an interpretation of the coefficient(s) is almost impossible. Therefore, a fundamental relationship has been deduced relating magnesium (Mg) extracted by conventional methods, $(Mg\text{-}ext)_a$, with Mg extracted by the 0.01 *M* $CaCl_2$ method $(Mg\text{-}ext)_{CaCl_2}$: $(Mg\text{-}ext)_a = \alpha + [\beta*(Mg\text{-}ext)_{CaCl_2,t=t}] + [\lambda*(Mg\text{-}ext)_{CaCl_2,t=t} * (Q\text{-}re)_{CaCl_2}]$. In

this relationship, α, β, and λ are related to characteristics of the extraction procedure and Mg-fractions in the soils. The $(Q\text{-}re)_{CaCl_2}$ is the actual cation exchange capacity of the soil during the $CaCl_2$ extraction. To test the usefulness of this relationship, 39 agricultural soils with widely differing soil characteristics were extracted with 0.01 *M* $CaCl_2$ and seven conventional Mg extractants. For six conventional methods, the explained variance of the fundamental relationships was more than 0.92. The explained variance of the relationship among 0.01 *M* $CaCl_2$ and the 0.1 *N* ammonium-lactate/0.4 *N* acetic acid extractant buffered at pH 3.75 was poor when the soils contained carbonates. We conclude that the derived fundamental relationship can be used for the design of a $CaCl_2$ soil testing program for Mg. Preferably, this $CaCl_2$ soil testing program should be validated in pot and field experiments.

INTRODUCTION

In a multinutrient soil extraction procedure, several elements or ions are extracted from a soil with one chemical reagent (= extractant). The introduction of a multinutrient extraction procedure in routine soil testing is attractive because it generates options for optimization of laboratory management and because the procedure is often cheaper as compared to a series of conventional single nutrient element extraction procedures (1). However, above all the introduction of a multinutrient extraction procedure should be justified by strong relationships between the amount of element or ion extracted and crop response. Houba et al. (2) found a good relationship between the results of the 0.01 *M* $CaCl_2$ extraction procedure and conventional extraction procedures for pH and for several plant nutrient elements. They assumed that if the amount of element or ion extracted by a conventional procedure is related to crop response, then the amount of element or ion extracted by the 0.01 *M* $CaCl_2$ procedure will also be related to crop response. Based on this assumption, Houba et al. (2) proposed to investigate the perspectives of the 0.01 *M* $CaCl_2$ procedure as a multinutrient extractant for routine soil testing. They suggested to convert conventional soil testing programs into a 0.01 *M* $CaCl_2$ soil testing program using the—mostly linear—relationships found between the amounts extracted by the two procedures.

In most comparative studies, the results of two extraction procedures are related using statistical techniques like (multiple) linear regression. Usually, however, the explained variance of the relationships is rather small. To increase the explained variance, soil characteristics like soil type, organic matter, clay, and carbonate contents are arbitrarily included (3–6). As a result, relationships may vary among studies although the same procedures and nutrient elements are com-

pared. Moreover, a soil chemical interpretation of the coefficients in the (multiple) linear regression equations remains obscure, which limits generalization of the results obtained. It is, therefore, questionable whether this type of relationships can be used for the design of a 0.01 *M* $CaCl_2$ soil testing program. The assessment of fundamental relationships deserves the highest priority. These fundamental relationships should take into account characteristics of the nutrient element, soil, extractant, and extraction procedure.

Magnesium is an important plant nutrient and several extractants are used in routine soil testing to determine the soil Mg status. Many of the conventional extractants for Mg use salt solutions and wide soil–solution ratios, suggesting that dissolution processes and cation exchange reactions between Mg and the added cation of the salt solution play an important role. The effect of dissolution and exchange processes on the composition of the soil solution are well-known and mathematically described. We think that the mathematical descriptions should be the basis of the fundamental relationships between Mg extracted by 0.01 *M* $CaCl_2$ and conventional procedures.

Dissolution and Exchange Chemistry of Magnesium

Magnesium is an essential nutrient element for plant growth and plant reproduction (7). Magnesium in soil includes soluble, readily exchangeable, slowly exchangeable and structural forms (8,9). The (water) soluble Mg forms, (Mg-sol), accounts for soil Mg present in the soil solution and in water soluble precipitates. The readily exchangeable Mg forms, (Mg-rex), comprise cationic Mg species in the diffuse layer electrostatically adsorbed to negatively charged soil particles. The slowly exchangeable Mg fraction, (Mg-sex), includes Mg specifically adsorbed to humic substances (10,11), (hydr)oxides (12) and clay minerals. The structural Mg forms, (Mg-str), includes Mg present in the lattices of clay minerals, in carbonates, etc. (13,14). Generally, (Mg-rex) is 3 to 20% of the total soil Mg content (15). Plant roots absorb Mg from the soil solution, thereby lowering the actual Mg concentration. However, the concentration of Mg in the soil solution is buffered by (Mg-rex) that, in turn, is slowly replenished by (Mg-sex) and (Mg-str) (7). Pot experiments in which soils were exhausted and Mg balance sheet studies of long-term field experiments, have shown that plant uptake of Mg is related to the size of (Mg-rex) (16–18). Routine Mg soil testing programs use salt solutions, acidified salt solutions or acid solutions as extractant to assess "plant-available Mg" (Table 1; 27). The cations or protons added via these extractants replace (part of) (Mg-rex) resulting in an increased Mg concentration in the solution immediately after addition (28). Depending on extraction time and the affinity of the (specific) adsorption site(s) for Mg and the added cation, Mg is also extracted from (Mg-sex). Acidified extractants may promote the dissolution

of structural forms like Mg containing carbonates and minerals (29). The extent of dissolution strongly depends on procedural aspects like proton activity, ionic strength, extraction time, and soil–solution ratio. When it is assumed that during soil extraction (Mg-sol) dissolves completely in the extractant, irrespective of the extraction procedure, then the total amount of Mg in the extractant solution after extraction, (Mg-ext), should equal the sum of (Mg-sol) and the changes of the other soil Mg fractions.

$$(\text{Mg-ext})_{a,t=t} = (\text{Mg-sol})_{t=0} + \sum_{i=1}^{i=3} \{(\text{Mg-}i)_{a,t=0} - (\text{Mg-}i)_{a,t=t}\} \qquad (1)$$

In Equation (1), $i = 1$ to $i = 3$ stands for (Mg-rex), (Mg-sex), and (Mg-str), respectively, expressed in mg kg^{-1} soil. The subscript a refers to the extraction procedure A and the subscripts $t = 0$ and $t = t$ to the time of start and termination of extraction, respectively.

Equation (1) can be worked out for two hypothetical extraction procedures A and B. At $t = 0$, (Mg-rex), (Mg-sex), and (Mg-str) will be the same irrespective of the extraction procedure. Then, subtraction of the results of B from A, gives:

$$(\text{Mg-ext})_{a,t=t} - (\text{Mg-ext})_{b,t=t} = \sum_{i=1}^{i=3} \{(\text{Mg-}i)_{b,t=t} - (\text{Mg-}i)_{a,t=t}\} \qquad (2)$$

Provided that the chemical processes and factors which determine the changes in (Mg-sex), (Mg-rex), and (Mg-str) at $t = t$ are known, Equation (2) can be used to derive a fundamental relationship for the difference in the amount of Mg extracted by the two procedures A and B.

The equivalent fraction of cations at the readily exchangeable adsorption sites of a soil is closely related to the activity of the cations in the soil solution at equilibrium in the soil suspension (29,30). Addition of cations to a soil in equilibrium will result in cation exchange processes at the readily exchangeable adsorption sites. In general, these exchange reactions are completed and in equilibrium within several minutes provided that the exchange process is not retarded by sterical hindering or diffusion controlled transport processes (31–33). In most soil testing programs, soil samples are gently crushed or milled to prevent possible physical/sterical blockades during extraction. Moreover, diffusion controlled processes in the soil suspension are (nearly) absent because soil samples are homogenized before extraction and because soil suspensions are prepared that have a wide soil–solution ratio and that are continuously stirred or shaken. Because these conditions prevail in most procedures we assume that a chemical equilibrium is attained in the soil suspension during extraction. The mathematical description of the equilibrium stage of an exchange reaction in which Mg adsorbed at the readily exchangeable adsorption sites is replaced by cation Z is given below (30).

$$(\text{E-rex})_{Mg} = \frac{((\text{E-rex})_Z)^{\frac{2}{m}} * [Mg] * f_{Mg}}{(K_{GT(S_2Mg \rightarrow S_mZ)})^2 * ([Z] * f_Z)^{\frac{2}{m}}} \quad (3)$$

In Equation (3), $(\text{E-rex})_{Mg}$ and $(\text{E-rex})_Z$ are the dimensionless fractions of Mg and Z, respectively, at the readily exchangeable adsorption site S; [Mg] and [Z] are the concentrations of these ions in the extractant solution in mol L^{-1}; f_{Mg} and f_Z represent their activity coefficients; and K_{GT} is the exchange coefficient for the exchange reaction in which Mg at site S is replaced by cation Z. This exchange reaction is described by $S_2Mg \rightarrow S_mZ$, m representing the valency of cation Z. For an extraction procedure A, [Mg] in Equation (3) equals $(\text{Mg-ext})_{a,t=t}$, divided by the added volume of the extractant, VOL_a in L kg^{-1} soil, and the atomic weight of Mg, M_{Mg} in g mol^{-1}. Equation (3) can thus be rewritten as follows:

$$(\text{E-rex})_{a,t=t,Mg} = \frac{((\text{E-rex})_{a,t=t,Z})^{\frac{2}{m}} * (\text{Mg-ext})_{a,t=t} * f_{a,Mg}}{(K_{GT(S_2Mg \rightarrow S_mZ)})^2 * ([Z_a] * f_{a,Z})^{\frac{2}{m}} * VOL_a * M_{Mg} * 1000} \quad (4)$$

In Equation (4) the subscript a refers to the extraction procedure A, the subscript $t = t$ to the time of termination of the extraction procedure A and the subscript Mg or Z to the cations Mg and Z that exchange during extraction procedure A. To calculate $(\text{Mg-rex})_{a,t=t}$, in mg kg^{-1} soil, $(\text{E-rex})_{a,t=t,Mg}$ should be multiplied with the charge of the readily exchangeable adsorption sites S during procedure A, $(\text{Q-re})_a$ in cmol(-) kg^{-1} soil, and M_{Mg} and divided by the valency of Mg. Equation (4) should then be rewritten as follows:

$$(\text{Mg-rex})_{a,t=t} = \frac{((\text{E-rex})_{a,t=t,Z})^{\frac{2}{m}} * f_{a,Mg} * (\text{Mg-ext})_{a,t=t} * (\text{Q-re})_a}{(K_{GT(S_2Mg \rightarrow S_mZ)})^2 * ([Z_a] * f_{a,Z})^{\frac{2}{m}} * VOL_a * 2 * 100} \quad (5)$$

Equation [5] is a mathematical description of the mutual dependency of $(\text{Mg-rex})_{a,t=t}$, soil characteristics ($(\text{Q-re})_a$, K_{GT}), characteristics of the extractant used in procedure A ($[Z_a]$, m, $f_{a,Mg}$ and $f_{a,Z}$) and procedural aspects (VOL_a). Equation (5) can be simplified into Equation (6),

$$(\text{Mg-rex})_{a,t=t} = \delta_a * (\text{Mg-ext})_{a,t=t} * (\text{Q-re})_a \quad (6)$$

in which δ_a equals Equation (7).

$$\delta_a = \frac{((\text{E-rex})_{a,t=t,Z})^{\frac{2}{m}} * f_{a,Mg}}{(K_{GT(S_2Mg \rightarrow S_mZ)})^2 * ([Z_a] * f_{a,Z})^{\frac{2}{m}} * VOL_a * 2 * 100} \quad (7)$$

Generally, the release of Mg from (Mg-sex) and (Mg-str) is kinetically determined. As a result, the soil suspension is mostly far from equilibrium. Without additional information on soil characteristics and kinetic aspects of the release processes during an extraction procedure A, it is impossible to estimate the amount $(\text{Mg-sex})_{a,t=t}$ and $(\text{Mg-str})_{a,t=t}$. Because extraction time of most Mg extraction procedures is relatively short, we assume that a very small and constant amount of Mg is extracted from $(\text{Mg-sex})_{t=0}$ and $(\text{Mg-str})_{t=0}$ during soil extraction, i.e., $(\text{CON-sex})_{a,t=t}$ and $(\text{CON-str})_{a,t=t}$, respectively. This results in:

$$(\text{Mg-sex})_{a,t=t} = (\text{Mg-sex})_{t=0} - (\text{CON-sex})_{a,t=t} \quad (8)$$

and,

$$(\text{Mg-str})_{a,t=t} = (\text{Mg-str})_{t=0} - (\text{CON-str})_{a,t=t} \quad (9)$$

The description of (Mg-rex), (Mg-sex), and (Mg-str) in Equations (7–9) can also be worked out for the procedures B and then for both procedures incorporated in Equation (2). Then, a mathematical description is obtained for a fundamental relationship for the difference in the amount of Mg extracted by the procedures A and B. Rearranging variables in this formulae yields Equation (10).

$$(\text{Mg-ext})_{a,t=t} = \alpha + [\beta * (\text{Mg-ext})_{b,t=t}] + [\lambda * (\text{Mg-ext})_{b,t=t} * (\text{Q-re})_b] \quad (10)$$

In Equation (10), α, β, and λ equal $\text{CON}/[1 + (\delta_a * (\text{Q-re})_a)]$, $1/[1 + (\delta_a * (\text{Q-re})_a)]$, and $\delta_b/[1 + (\delta_a * (\text{Q-re})_a)]$, respectively. CON is a constant and equals the sum of $(\text{CON-sex})_{a,t=t} - (\text{CON-sex})_{b,t=t}$ and $(\text{CON-str})_{a,t=t} - (\text{CON-str})_{b,t=t} \cdot \delta_b$ equals Equation (7) worked out for procedure B.

The aim of the experiments described below is to evaluate Equation (10) as a useful tool to relate the amount of Mg extracted by a conventional Mg extraction procedure and the 0.01 *M* $CaCl_2$ procedure.

MATERIALS AND METHODS

Thirty-nine soil samples with widely differing soil characteristics were collected from the plough layer of agricultural fields in The Netherlands. The fresh soil samples were pretreated according to ISO 11464 (34). Within the framework of an EC–Copernicus project (35) the 39 soils were extracted in The Netherlands, Hungary, Poland, and the Czech Republic according to current soil testing procedures for Mg in the respective countries (Table 1). Six unbuffered salt solutions and two acidified salt solutions were tested. The Mg concentration in the supernatant was measured by atomic absorption spectrophotometry (AAS) in all countries. The actual cation exchange capacity (CEC) of the soil was determined with the unbuffered $BaCl_2$ method (24), the clay content according NEN 5753 (36),

Table 1. Summary of the Prevailing Soil Extraction Methods for Magnesium

Procedure	Extractant	Country	Soil/Solution Ratio (w/v)	Shaking Time	References
Unbuffered Salt Solutions					
0.01 *M* $CaCl_2$	0.01 *M* $CaCl_2$	The Netherlands	1:10	2 h	Houba et al. (19)
Schacht I	0.0125 *M* $CaCl_2$	Poland	1:10	2 h	Schachtschabel (20)
Schacht II	0.0125 *M* $CaCl_2$	Czech Republic	1:10	1 h	Zbiral (21)
NaCl	0.5 *M* NaCl	The Netherlands	1:5	1 h	Ferrari and Sluijsmans (22)
KCl	1 *M* KCl	Hungary	1:2.5	2 h	Mazaeva (23) (slightly modified)
$BaCl_2$	0.1 *M* $BaCl_2$	The Netherlands	1:12 (3× repeated)	1 h	ISO 11260 (24)
Acidified Salt Solutions					
Amlac	0.1 *N* NH_4-lactate + 0.4 *N* acetic acid buffered at pH 3.75	Hungary	1:20	2 h	Egnér et al. (25)
Mehlich II	0.2 *M* NH_4Cl + 0.2 *M* acetic acid + 0.015 *M* NH_4F + 0.12 *M* HCl	Czech Republic	1:10	10 min	Mehlich (26)

Table 2. Soil Characteristics of the 39 Samples from Agricultural Soils in The Netherlands

	Minimum	Maximum	Average
Soil characteristics			
pH KCl	4.0	7.5	5.7
Clay content (%)	2	52	15
Organic carbon content (%)	0.6	8.3	2.6
Carbonate content (%)	0	8.27	0.78
Volume weight ($g\ l^{-1}$)	1069	1479	1291
Cation exchange capacity, cmol(-) (kg^{-1})	2.1	40.3	13.8
Mg extracted by the procedures (mg kg^{-1})			
0.01 *M* $CaCl_2$	18	287	120
Schacht I	24	318	128
Schacht II	12	238	91
NaCl	20	312	140
KCl	13	350	126
$BaCl_2$	21	494	195
Amlac	12	810	222
Mehlich II	23	456	183

pH-KCl according to ISO 10390 (37), the organic carbon content according ISO 14235 (38), and carbonate content (% $CaCO_3$) according to NEN 5757 (39). Table 2 shows the soil characteristics and the results of tested Mg extraction procedures. Statistical analysis were carried out using the computer program Genstat 5 (40). Equation (11) was used for linear regression analysis.

$$(\text{Mg-ext})_{a,t=t} = \kappa + \mu * (\text{Mg-ext})_{CaCl_2,t=t} \tag{11}$$

In Equation (11), Mg extracted by the 0.01 *M* $CaCl_2$ procedure, $(\text{Mg-ext})_{CaCl_2,t=t}$, was the explanatory variable and Mg extracted by the conventional procedure, $(\text{Mg-ext})_{a,t=t}$, the response variable; κ equals the intercept of the regression line with the *Y*-axis and μ equals the slope of the regression line. The multiple linear regression analysis was carried out according $(\text{Mg-ext})_{a,t=t} = \alpha + \beta * (\text{Mg-ext})_{CaCl_2,t=t} + [\lambda * (\text{Mg-ext})_{CaCl_2,t=t} * (\text{Q-re})_{CaCl_2}]$. In this analysis, $(\text{Mg-ext})_{CaCl_2,t=t}$ and $(\text{Mg-ext})_{CaCl_2,t=t} * (\text{Q-re})_{CaCl_2}$ were the explanatory variables and $(\text{Mg-ext})_{a,t=t}$ the response variable; α equals the intercept of the regression line with the *Y*-axis and β and λ are coefficients of the response variables. Confidence intervals of the coefficients in the (multiple) linear regression equations were determined at $P = 0.05$.

In the multiple regression analysis it was assumed that the charge of the readily exchangeable adsorption sites during the $CaCl_2$ extraction procedure, $(\text{Q-re})_{CaCl_2}$, equaled the actual CEC.

RESULTS AND DISCUSSION

Statistical Analysis

The explained variance (R^2) of the simple linear relationships between the $CaCl_2$ procedure and one of the seven conventional procedures varied from 0.01 for the $CaCl_2$–Amlac relationship to more than 0.97 for the $CaCl_2$–Schacht(I) relationship (Table 3).

The low R^2 of the $CaCl_2$–Amlac relationship suggests that the mechanism of Mg extraction is different for $CaCl_2$ and Amlac. Except for the $CaCl_2$–Amlac relationship, the intercept κ of the linear relationships is not significantly different from zero. When the intercept κ is significantly different from zero it means that one of the procedures extract Mg from a soil Mg fraction which is not extractable for the other procedure. When $\mu = 1$, an increase of Mg extracted by 0.01 *M* $CaCl_2$ equals the increase of Mg extracted by the conventional procedure. This means that both procedures extract Mg from the same soil Mg fractions and that both procedures are equally effective in Mg extraction. When μ is significantly smaller or higher than 1, the conventional procedure is less or more effective, respectively, in extracting Mg compared to $CaCl_2$. Table 3 shows that μ is significantly smaller than 1 for the $CaCl_2$–Schacht(II) relationship, not significantly different from 1 for the $CaCl_2$–KCl relationship and significantly higher than 1 for the relationships relating $CaCl_2$ with Schacht(I), sodium chloride (NaCl), barium chloride ($BaCl_2$), and Mehlich.

The R^2 of the multiple regression relationships was found to be equal or higher than R^2 of the comparable simple linear relationships (Table 3). Improvement of R^2 is considerable for the $CaCl_2$–Amlac, $CaCl_2$–KCl, $CaCl_2$–Mehlich, $CaCl_2$–$BaCl_2$, and $CaCl_2$–NaCl relationships. Improvement is negligible for the $CaCl_2$–Schacht(I) and $CaCl_2$–Schacht(II) relationships, reflecting that both the type of extractant and procedural aspects of Schacht(I), Schacht(II), and $CaCl_2$ are comparable. Except for the $CaCl_2$–Amlac relationship (Table 3), all relationships have high R^2 values, higher than 0.92, indicating that Equation (10) and its explanatory variables $(\text{Mg-ext})_{CaCl_2,t=t}$ and $(\text{Mg-ext})_{CaCl_2,t=t} * (\text{Q-re})_{CaCl_2}$ can be used to relate the amount of Mg extracted by $CaCl_2$ and conventional procedures.

Coefficient β

In Equation [10], β equals $1/[1 + (\delta_a * (\text{Q-re})_a)]$. From Equation (6) it follows that $[\delta_a * (\text{Q-re})_a]$ equals the ratio $(\text{Mg-rex})_{a,t=t}/(\text{Mg-ext})_{a,t=t}$. When $[\delta_a * (\text{Q-re})_a]$ is replaced by $(\text{Mg-rex})_{a,t=t}/(\text{Mg-ext})_{a,t=t}$, β equals Equation (12).

$$\beta = \frac{(\text{Mg-ext})_{a,t=t}}{(\text{Mg-ext})_{a,t=t} + (\text{Mg-rex})_{a,t=t}} \qquad (12)$$

Table 3. Results of the Statistical Analysis of the Simple Linear Relationship $(\text{Mg-ext})_{a,t=t} = \kappa + \mu * (\text{Mg-ext})_{CaCl_2,t=t}$ and the Multiple Linear Relationship $(\text{Mg-ext})_{a,t=t} = \alpha + \beta * (\text{Mg-ext})_{CaCl_2,t=t} + [\lambda * (\text{Mg-ext})_{CaCl_2,t=t} * (\text{Q-re})_{CaCl_2}]$ (See Equation (10)). R^2 is the Explained Variance of the Relationships Found. The Standard Error of the Estimates κ, μ, α, β, and λ Are Given Between Parentheses

Conventional Procedure	Simple			Multiple			
	κ	μ	R^2	α	β	λ	R^2
Schacht(I)	−0.44 (4.43)	1.066 (0.032)	0.97	0.54 (4.52)	1.034 (0.044)	0.0015 (0.0014)	0.97
Schacht(II)	−2.80 (5.30)	0.780 (0.039)	0.92	−3.73 (5.42)	0.812 (0.053)	−0.0015 (0.0010)	0.92
NaCl	−4.10 (10.10)	1.193 (0.074)	0.88	6.73 (5.17)	0.830 (0.051)	0.0170 (0.0016)	0.97
KCl	−18.80 (14.10)	1.200 (0.103)	0.79	−4.09 (7.84)	0.708 (0.077)	0.0231 (0.0025)	0.94
$BaCl_2$	−8.20 (21.20)	1.688 (0.155)	0.76	17.74 (3.61)	0.820 (0.035)	0.0407 (0.0011)	0.99
Amlac	190.10 (56.80)	0.267 (0.415)	0.01	222.25 (52.20)	−0.820 (0.511)	0.0510 (0.0164)	0.22
Mehlich	−1.50 (21.00)	1.531 (0.154)	0.73	22.65 (8.18)	0.722 (0.080)	0.0379 (0.0026)	0.96

When procedure A is effective in replacing Mg from the readily exchangeable sites, then $(Mg\text{-}rex)_{a,t=t}$ is relatively small and $(Mg\text{-}ext)_{a,t=t}$ relatively large and as a result β should approach the value 1. When procedure A is ineffective in replacing (Mg-rex) than $(Mg\text{-}ext)_{a,t=t}$ will be small and β will approach zero. Thus, β is an indicator of "the extracting power" of procedure A of Mg from (Mg-rex). Indicator β theoretically ranges from 0 to 1. The results for the multiple relationships in Table 3 show that β varies from -0.820 for the $CaCl_2$–Amlac relationship to 1.034 for the $CaCl_2$–Schacht(I) relationship. The β of the $CaCl_2$–Amlac relationship is negative, but not significantly different from 0. This low value suggests that Amlac extracts almost no Mg from the readily exchangeable sites or that the assumptions underlying Equation (10) are not correct. The β of the $CaCl_2$–Schacht(I) relationship is not significantly different from 1 and suggests a complete exchange of Mg at the readily exchangeable sites. The β of the other relationships varied from 0.71 to 0.83.

The experimental results showed that Schacht(II) extracted less Mg from the test soils than Schacht(I). In the $CaCl_2$–Schacht(I) relationship, β was significantly higher than β found in the $CaCl_2$–Schacht(II) relationship and equal to the theoretical maximum of 1. When the exchange of calcium (Ca) for Mg at the readily exchangeable adsorption sites is instantaneous, and when β is a characteristic of the conventional extraction procedure A, then β of Schacht(I) and Schacht(II) should be of the same order of magnitude because both methods only differ in shaking time, 2 and 1 h, respectively. The observed significant difference in β suggests that shaking time is an important factor. An effect of shaking time has also been observed by van Erp et al. (41). They found that the amount of Mg extracted by the $CaCl_2$ procedure continued to increase up to an extraction period of 2 h. This suggests that the exchange process of Mg for Ca is kinetically determined for part of the exchange sites. Figure 1 shows that the difference between Mg extracted by the Schacht(I) and Schacht(II) procedure in the present study tends to increase when the organic carbon (C) content of the soil increases. This means that during the second hour of the extraction period Schacht(I) extracts Mg from a slowly exchangeable Mg fraction (Mg-sex) related to organic C. When it is assumed that a (pseudo-) equilibrium exist among Mg concentration in the solution and Mg that resides at (Mg-rex) and (Mg-sex) after a 2 h shaking period (41), then the Gaines–Thomas approach is also valid for the derivation of a causal relationship between $(Mg\text{-}ext)_{a,t=t}$ and $(Mg\text{-}sex)_{a,t=t}$. Hence, an equation $(Mg\text{-}sex)_{a,t=t}$ comparable to Equation (5) will be found. This new equation can be incorporated in Equation (2) together with the original $(Mg\text{-}rex)_{a,t=t}$ and $(Mg\text{-}str)_{a,t=t}$. Rearranging this new Equation (2) will result in an equation similar to Equation (10) in which β includes characteristics of both the readily and slowly exchangeable fraction. Because of that β of the $CaCl_2$–Schacht(I) procedure may equal 1. The β of the $CaCl_2$–Schacht(II) relationship will be smaller than 1 because a much smaller amount of Mg is extracted from (Mg-sex).

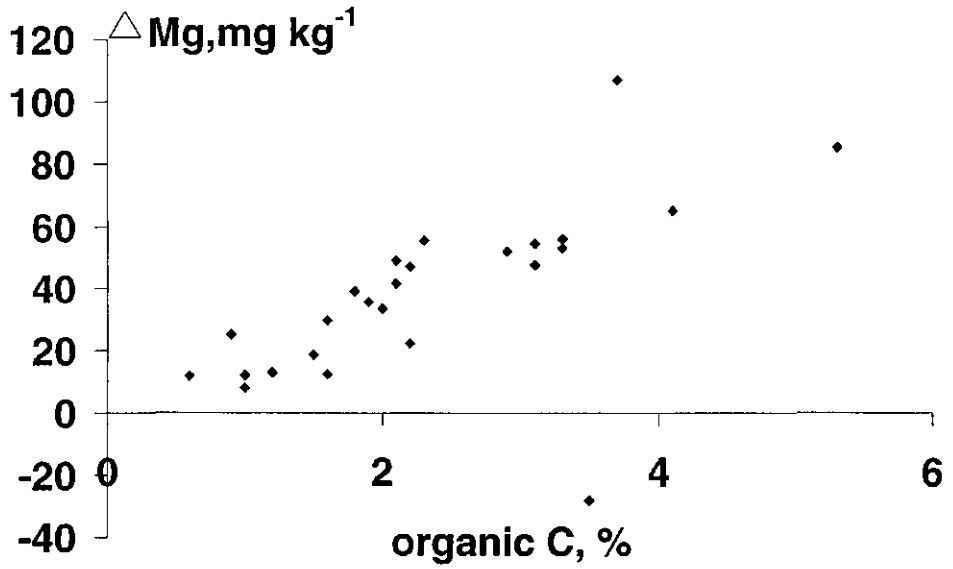

Figure 1. Relationship between the organic C content, % C, of the test soils with a pH-$CaCl_2$ larger than 5 and the difference in Mg extracted by Schacht(I) and Schacht(II).

Coefficient α

According to Equation (10), α equals CON/[1 + (δ_a * (Q-re)$_a$)]. Since β equals 1/[1 + (δ_a * (Q-re)$_a$], α can also be written as CON * β. When no Mg is extracted from (Mg-sex) or (Mg-str) then CON is nil and α will not be significantly different from 0. Is Mg extracted from (Mg-sex) or (Mg-str) then CON as well as α will be significantly different from zero provided β is significantly different from zero. The statistical analysis (Table 3) shows that the $CaCl_2$–Mehlich, $CaCl_2$–Amlac, and $CaCl_2$–$BaCl_2$ relationships have an intercept α significantly higher than 0. The intercept α of the $CaCl_2$–Amlac relationship is much higher than for the $CaCl_2$–Mehlich and $CaCl_2$–$BaCl_2$ relationships. The Mehlich and Amlac procedures use acidified extractants which may dissolve, e.g., Mg-calcites, present in carbonate containing soils. As the dissolution of carbonates is kinetically determined (42,43), the (unbuffered) proton activity and short extraction period of the Mehlich extractant may be insufficient to dissolve the same amount of carbonates as the Amlac procedure. When the difference in Mg extracted among Amlac and Mehlich, ΔMg, results from the dissolution of extra carbonates by Amlac, then also extra Ca should be extracted by Amlac compared to Mehlich, ΔCa. Figure 2 shows the linear relationship among ΔCa and ΔMg. The slope of the regression line is highly significant (standard error = 0.01) and suggests that the Ca/Mg composition of the dissolved carbonates is more or less the same in the different test soils. A ratio of Ca and Mg in carbonates of 0.05, i.e., 100:5,

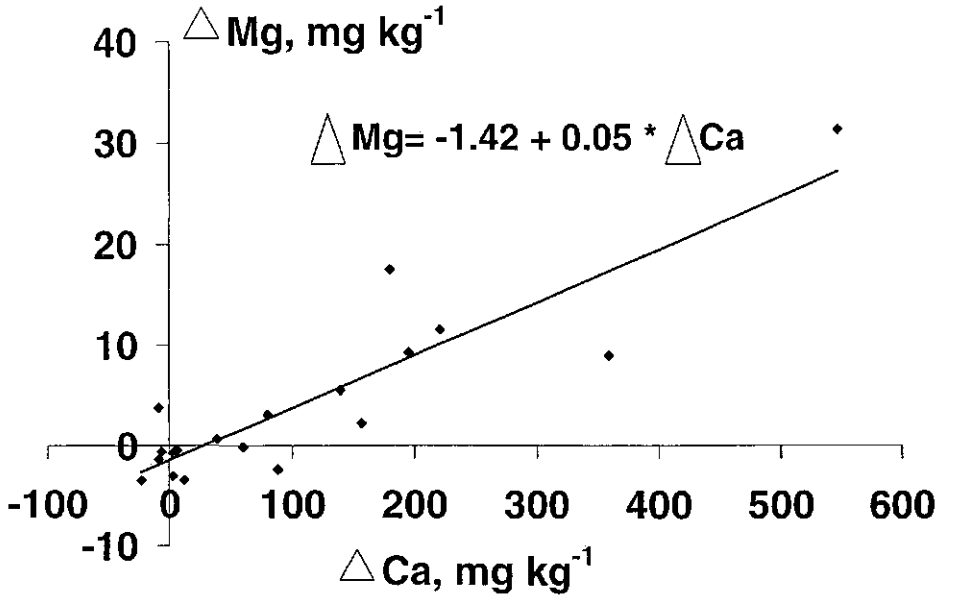

Figure 2. Relationship between ΔCa, the difference in Ca extracted between Amlac and Mehlich, and ΔMg, the difference in Mg extracted between Amlac and Mehlich. Calculated for the carbonate containing test soils.

falls in the range of Ca/Mg ratios for soil Mg-calcites and magnesium limestone (44). When the carbonate containing test soils were left out in the multiple linear regression analysis α was not significantly different from zero for the $CaCl_2$–Mehlich and $CaCl_2$–Amlac relationships (data not shown). We conclude that acid extractants may dissolve Mg containing soil carbonates increasing the amount of Mg extracted. Kinetic aspects of the carbonate dissolution and procedural aspects determine the actual amount of Mg extracted. The $BaCl_2$ procedure uses a repeated extraction with barium (Ba^{2+}) ions to extract Mg from soil fractions. Since the dehydration energy of Ba^{2+} is relatively low compared to other cations, an inner-sphere adsorption of Ba^{2+} is possible. Then, Ba^{2+} may replace cations (specifically) adsorbed to humic substances and at the surface of clay minerals, oxides and carbonates (45) and may even replace cations from the interlayer of clay minerals. The cation potassium (K^+) ions in the KCl extractant will replace cations adsorbed at the surface of clay minerals but also from the interlayer of clay minerals. Therefore, the difference among Mg extracted by the $BaCl_2$ and KCl procedure, may originate from Mg specifically adsorbed at humic substances, oxides or carbonates. Analysis of the difference in Mg extracted among $BaCl_2$ and KCl showed that the difference was related to the clay content of the soils (not shown here) and not to the organic C content or carbonate content. Since, the (hydr)oxide content of soils is positively related to the clay content, Ba^{2+} may have replaced

Mg specifically adsorbed at the surface of these (hydr)oxides which is not replaceable by K at high pH (12). We conclude that α in the $CaCl_2$–$BaCl_2$ relationship is larger than 0 because $BaCl_2$ replace Mg from an unknown slowly exchangeable Mg-fraction related to the soil clay faction.

Coefficient λ

Coefficient λ in Equation (10) equals $\delta_{CaCl_2}/[1 + (\delta_a * (Q\text{-re})_a)]$. As shown, $1/(1 + (\delta_a * (Q\text{-re})_a)]$ equals β which is an indicator of "the extracting power" of procedure A. According to Equation (6), δ_{CaCl_2} equals $(Mg\text{-rex})_{CaCl_2,t=t}/[(Mg\text{-ext})_{CaCl_2,t=t} * (Q\text{-re})_{CaCl_2}]$. This means that λ is an integration of the effect of i) the extraction power of procedure A, ii) the actual CEC of the test soil during $CaCl_2$ extraction, and iii) the extraction characteristics $(Mg\text{-rex})_{CaCl_2,t=t}$ and $(Mg\text{-ext})_{CaCl_2,t=t}$ of the $CaCl_2$ procedure. Since the constituents of λ are equal to or larger than 0, the theoretical minimum of λ is 0. When two or more relationships have comparable values for λ, "the extracting power" of the conventional procedures must be comparable since $(Mg\text{-rex})_{CaCl_2,t=t}$, $(Mg\text{-ext})_{CaCl_2,t=t}$, and $(Q\text{-re})_{CaCl_2}$ are fixed values when two relationships are compared. This holds for the $CaCl_2$–KCl and $CaCl_2$–NaCl, $CaCl_2$–Mehlich and $CaCl_2$–$BaCl_2$, and the $CaCl_2$–Schacht(I) and $CaCl_2$–Schacht(II) relationships.

Evaluation

Fundamental relationships exists between the $CaCl_2$-procedure and conventional procedures for Mg. The relationships are based on the extraction of Mg from Mg fractions in the soil. These fundamental relationships are a reliable basis for the conversion of conventional soil testing programs for Mg into a 0.01 *M* $CaCl_2$ soil testing program for Mg. The fundamental relationship require additional information on (Q-re) of the test soils during the $CaCl_2$-procedure. The actual CEC, determined through the unbuffered $BaCl_2$ extraction, can be used for this. Determination of the actual CEC necessitates the execution of an extra analytical procedure. Therefore, the perspectives of calculating the actual CEC on the basis of pH and content of organic matter and clay of the soil should be investigated. Field and pot and field experiments are necessary subsequently to test the $CaCl_2$ soil testing program for Mg in practice.

CONCLUSIONS

The fundamental relationship $(Mg\text{-ext})_{CaCl_2,t=t} = \alpha + \beta * (Mg\text{-ext})_{CaCl_2,t=t} + [\lambda * (Mg\text{-ext})_{CaCl_2,t=t} * (Q\text{-re})_{CaCl_2}]$ can be used for conversion of conventional soil testing programs for Mg into a $CaCl_2$ soil testing program for Mg. However,

the fundamental relationship cannot be applied to carbonate containing soils when acidified extractants buffered at a relatively low pH are used.

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CHAPTER 6

ACTUAL CATION EXCHANGE CAPACITY OF AGRICULTURAL SOILS AND ITS RELATIONSHIP WITH PH AND CONTENT OF ORGANIC CARBON AND CLAY

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ACTUAL CATION EXCHANGE CAPACITY OF AGRICULTURAL SOILS AND ITS RELATIONSHIP WITH pH AND CONTENT OF ORGANIC CARBON AND CLAY

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ABSTRACT

For the set up of a multinutrient 0.01 *M* calcium chloride ($CaCl_2$) soil testing program a conversion from conventional soil testing programs to a $CaCl_2$ program has been proposed in literature. Such conversion should be based on the relationship between test values of the conventional method and the $CaCl_2$ method. For magnesium (Mg) it was shown in earlier work that the conversion could be improved when the actual cation exchange capacity (CEC) of the soil, CEC_{act}, was taken into account. However, determination of CEC_{act} necessitates an extra analytical procedure. The goal of this study was to test a procedure for estimating CEC_{act} of a soil. In this procedure, CEC_{act} was calculated as the summation of the esti-

mated charge of organic carbon (C) and clay in the soil at pH_{act}, the actual pH of the soil. A series of 39 test soils representing agricultural soils in The Netherlands was used to derive the pH dependency of the negative charge of organic C and clay. The following relationship was found: CEC_{act}: $[M(1)\times 0.0624] + [M(2)\times(0.295-D(2)_{pHact})]$. In this relationship, $M(1)$ and $M(2)$ represent clay and organic C in g kg^{-1} dry soil, respectively, and $D(2)_{pHact}$ the difference in negative charge of organic C at pH_{act} and pH 8.1. The pH_{act} equals pH measured in 0.01 *M* $CaCl_2$. The relationship was tested on another dataset of 38 agricultural soils. There was good agreement between the calculated and measured CEC_{act} ($R^2=0.89$). It was concluded that the procedure can be used for estimation of CEC_{act}.

INTRODUCTION

Soil testing is an important tool for optimization of fertilization and soil fertility status of agricultural soils. The perspectives of the use of 0.01 *M* $CaCl_2$ as a multinutrient soil extractant in soil testing are good (1). Already Houba et al. (2) suggested to convert conventional soil testing programs for nutrient elements and pH into a 0.01 *M* $CaCl_2$ multinutrient soil testing program. This conversion should be based on the relationship found between test values of the 0.01 *M* $CaCl_2$ extractant and conventional extractants. For Mg it was shown that the relationship between Mg extracted by 0.0l *M* $CaCl_2$ and Mg extracted by six conventional Mg extraction procedures improved significantly when the actual cation exchange capacity, CEC_{act}, of the soil was taken into account (3). The CEC_{act} was measured according to the unbuffered 0.01 *M* barium chloride ($BaCl_2$) procedure (ISO 11260, 1994) yielding the CEC at a pH and ionic strength (*I*) comparable to normal field conditions. This method is a slight modification of the compulsive exchange method as originally proposed by Gillman (4). Since the determination of CEC_{act} requires an extra analytical procedure it was proposed to investigate the perspectives of calculating CEC_{act} on the basis of soil characteristics like pH and the content of soil organic carbon and clay (fraction <2 mm).

The CEC of a soil is defined as the total sum of exchangeable cations that a soil, soil constituent, or other material can adsorb at a specific pH (5). This adsorption results from the negative charge of clay minerals, organic matter or organic C and (hydr)oxides in the soil (6). The negative charge may depend on pH and *I*. The CEC is often written as the summation of the negative charge of soil constituents according to Equation (1).

$$\mathrm{CEC} = \sum_{x=1}^{x=3} Q(x) \qquad (1)$$

In Equation (1), CEC is the negative charge of the soil in cmol(−) kg^{-1} dry soil, Q the negative charge of the soil constituent in cmol(−) kg^{-1} dry soil, and $x=1$, 2, and 3 represent the soil constituents clay minerals (<2 μm), organic C and (hydr)oxides, respectively. The $Q(x)$ can be written as the multiplication of the mass weight $M(x)$ and negative charge $R(x)$ of soil constituent x according to Equation (2).

$$Q(x) = M(x) \times R(x) \qquad (2)$$

In Equation (2), $M(x)$ is expressed in g soil constituent kg^{-1} dry soil and $R(x)$ in cmol(−) g^{-1} soil constituent. The $R(1)$, the negative charge of clay minerals, may vary from practically zero to more than 0.200 cmol(−) g^{-1} (6,7). The $R(1)$ of, e.g., 2:1 layer type clay minerals, is independent of pH and ionic strength (I) because the negative charge results from an isomorphic substitution of cations in the mineral lattice. In contrast, $R(1)$ of, e.g., 1:1 layer type clay mineral depends on pH and I because hydrogen (H) dissociation and association characteristics of exposed surface-OH-groups depend on pH and I (6). Generally, the clay fraction of soils is a mixture of (crystallic and or amorphous) 1:2 and 1:1 clay minerals. Therefore, an effect of pH (and I) on $R(1)$ cannot be excluded (8,9).

The $R(2)$, the negative charge of organic C, mainly originates from the ionization of H from carboxyl-(COOH) and phenolic OH groups (10). The magnitude of the negative charge of these functional groups is positively related to soil pH in the pH range from 3.0 to 8.0, and to the ionic strength I of the solution (10,11). Beyond the pH range from 3.0 to 8.0, the negative charge is more or less constant. The effect of I is maximal between pH 4.0 and 6.0 and negligible at about pH 3.0 and 8.0 (11). An effect of pH on $R(2)$ of organic C in soils is often found (8,12,13).

The $R(3)$, the negative charge of soil (hydr)oxides, mainly (amorphous) iron- and aluminum-(hydr)oxides, originates from surface-OH-groups which may adsorb hydrogen (H^+) or hydronium (OH^-) ions. Not all surface-OH-groups adsorb H^+ and OH^- at the same pH. Generally, Fe- and Al-(hydr)oxides become net negatively charged at a pH above 7.7 (6). Comparable to $R(2)$ the negative charge of (hydr)oxides increases when pH and I increase.

Summarizing, $R(x)$ may depend on pH and I, and therefore $R(x)$ in Equation (2) should be estimated at the I and pH of the soil under field conditions. In this study, it is assumed that the average I of soil solutions is 0.03 M which equals the ionic strength of 0.01 M $CaCl_2$. The actual pH of a soil, pH_{act}, is assumed to be equal to the pH measured in 0.01 M $CaCl_2$. In literature the contribution of (hydr)oxides, $Q(3)$, to the CEC_{act} is often neglected in the pH range of 4.0 to 8.0 because $R(3)$ of pure Fe- and Al-(hydr)oxides gets net negatively charged above

pH 7.7 (6). Moreover, there is little insight in the (hydr)oxide content of soils mainly because a cheap, common soil testing method for determination of soil (hydr)oxide content is lacking. When $R(3)$ is neglected, then Equation (3) provides a mathematical description of the relationship between CEC_{act} and the clay content $M(1)$, organic C content $M(2)$, and $R(1)$ and $R(2)$ at pH_{act} and $I=0.03$ M.

$$CEC_{act} = M(1) \times R(1)_{pHact,I=0.03} + M(2) \times R(2)_{pHact,I=0.03} \quad (3)$$

The aim of this paper is to test Equation (3) for estimation of CEC_{act}.

MATERIALS AND METHODS

Thirty-nine soil samples with widely differing soil characteristics were collected from the plough layer of agricultural fields in The Netherlands. The selected soils represent the major agricultural soils in The Netherlands. The fresh soil samples were pretreated according to ISO 11464 (14).

The actual cation exchange capacity ($CEC_{pHact,I=0.03}$) of the test soils was determined according to the unbuffered 0.01 M $BaCl_2$ method (15). The potential CEC, $CEC_{8.1,I=0.3}$, was determined according the 0.1 M $BaCl_2$ method buffered at pH 8.1 (16). The clay content of the test soils, $M(1)$, was determined according to NEN 5753 (17), the organic C content, $M(2)$, according to ISO 14235 (18), and pH_{act} according to the 0.01 M $CaCl_2$ procedure (19). Table 1 gives an overview of the soil characteristics.

To estimate CEC_{act} according to Equation (3), $R(1)_{pHact,I=0.03}$ and $R(2)_{pHact,I=0.03}$ of the soil should be known. This requires knowledge of the relationship between $R(1)$ and $R(2)$ with pH at $I=0.03$ M. However, this relationship is soil specific and difficult to attain. Therefore, a general $R(1)_{pH,I=0.03}$ and $R(2)_{pH,I=0.03}$ relationship was deduced in four steps.

Table 1. Soil Characteristics of the 39 Samples from Agricultural Soils in The Netherlands

Soil Characteristics	Minimum	Maximum	Average
pH-$CaCl_2$	4.2	7.5	5.7
Clay content (%)	2	52	15
Organic carbon (%)	0.6	8.3	2.6
CEC_{act} (cmol(−) kg^{-1})	2.1	40.3	13.8
Potential CEC (cmol(−) kg^{-1})	6.5	44.6	19.7

Comparable to CEC_{act} in Equation (3), Equation (4) gives the mathematical description of the potential CEC ($CEC_{8.1,I=0.3}$):

$$CEC_{8.1,I=0.3} = M(1) \times R(1)_{8.1,I=0.3} + M(2) \times R(2)_{8.1,I=0.3} \quad (4)$$

In the Netherlands, 2:1 layer type minerals like illites and smectites are the predominant clay minerals in soils. The negative charge of the minerals originates from an isomorphic substitution in the mineral lattice, and is, therefore, not affected by I. In contrast, the negative charge of organic C depends on I, but at pH values of about 8.0 the effect of I is negligible (11). Then, $CEC_{8.1,I=0.3}$ in Equation (4) can be replaced by $CEC_{8.1,I=0.03}$ as well as $R(1)_{8.1,I=0.3}$ and $R(2)_{8.1,I=0.3}$ by $R(1)_{8.1,I=0.03}$ and $R(2)_{8.1,I=0.03}$, respectively. Subtraction of Equation (3) from the modified Equation (4) gives Equation (5).

$$\begin{aligned} CEC_{8.1,I=0.03} - CEC_{pHact,I=0.03} &= \Delta CEC \\ &= M(1) \times D(1) + M(2) \times D(2) \end{aligned} \quad (5)$$

Equation (5) shows that the difference in CEC of a soil at pH 8.1 and pH_{act} is a function of $M(1)$ and $M(2)$ and $D(1)$ and $D(2)$. The $D(1)$ equals the difference between $R(1)_{8.1,I=0.03}$ and $R(1)_{pHact,I=0.03}$ and $D(2)$ equals the difference between $R(2)_{8.1,I=0.03}$ and $R(2)_{pHact,I=0.03}$. Both are expressed in cmol(−) g^{-1} soil constituent. Re-arranging Equation (5) gives Equation (6):

$$\frac{\Delta CEC}{M(1)} = D(1) + \frac{M(2)}{M(1)} \times D(2) \quad (6)$$

It follows from Equation (6) that $D(1)$ and $D(2)$ of a soil equal the intercept and slope, respectively, of the linear relationship between $M(2)/M(1)$ as the explanatory variable and $\Delta CEC/M(1)$ as the response variable. In this study, Equation (6) and the experimental data of the 39 test soils were used to relate $D(1)$ and $D(2)$ to pH_{act}. First of all, the 39 test soils were arranged in ascending pH_{act} order. Then $D(1)$ and $D(2)$ were estimated as a moving estimate of six successive test soils using Equation (6) and linear regression analysis. Moreover, pH_{act} was calculated as the average pH of the six test soils. In this way, 34 [pH_{act}, $D(1)$] and 34 [pH_{act}, $D(2)$] data combinations were obtained. The choice of grouping six test soils was arbitrary. When soils were grouped in less than six successive test soils then the confidence intervals of the estimates of $D(1)$ and $D(2)$ were large. However, then pH_{act} as an estimate of the average pH of the six soils was reliable. The opposite occurred when more than six test soils were grouped.

Step 2

In Step 1, 34 [pH_{act}, $D(1)$] and 34 [pH_{act}, $D(2)$] data combinations were deduced. The relationship between pH_{act} and $D(x)$ was fitted using curve fitting techniques in the statistical computer program Genstat 5 (20).

Step 3

The $R(x)_{pHact,I=0.03}$ equals the summation of $R(x)_{8.1,I=0.03}$ and $D(x)_{pHact}$ according to Equation (7):

$$R(x)_{pHact,I=0.03} = -D(x)_{pHact} + R(x)_{8.1,I=0.03} \quad (7)$$

In Equation (7), $D(x)_{pHact}$ equals $D(x)$ at pH_{act} which can be estimated with the relationship found in Step 2. Filling in Equation (7) in Equation (3) gives Equation (8).

$$\begin{aligned} CEC_{act} = {} & M(1) \times [-D(1)_{pHact} + R(1)_{8.1,I=0.03}] \\ & + M(2) \times [-D(2)_{pHact} + R(2)_{8.1,I=0.03}] \end{aligned} \quad (8)$$

Re-arranging Equation (8) gives Equation (9).

$$\frac{CEC_{act} + M(1) \times D(1)_{pHact} + M(2) \times D(2)_{pHact}}{M(1)} = R(1)_{8.1,I=0.03} + \frac{M(2)}{M(1)} \times R(2)_{8.1,I=0.03} \quad (9)$$

From Equation (9) it follows that $R(1)_{8.1,I=0.03}$ and $R(2)_{8.1,I=0.03}$ equal the intercept and slope, respectively, of the linear relationship between $M(2)/M(1)$ as the explanatory variable and left hand side of Equation (9) as the response variable. The experimental data of the 39 test soils were used to estimate $R(1)_{8.1,I=0.03}$ and $R(2)_{8.1,I=0.03}$ using linear regression analysis.

The negative charge of organic C and clay at pH 8.1 was also estimated via multiple linear regression using $M(1)$, $M(2)$, and the potential CEC measured according the buffered $BaCl_2$ method (I=0.3).

Step 4

The $R(x)_{pH,I=0.03}$ relationships can be obtained by filling in i) the estimate $R(x)_{8.1,I=0.03}$ (Step 3) and ii) the relationship between $D(x)$ and pH_{act} (Step 2) in Equation (7). The $R(x)_{pH,I=0.03}$ relationships obtained can be filled in in Equation (3).

The usefulness of Equation (3) for estimation for CEC_{act} was tested by comparing the measured and calculated CEC_{act} of the 39 test soils and an extra data set of 38 agricultural soils from The Netherlands. Statistical analyses were carried out using the computer program Genstat 5 (20). Differences between estimates were tested at $P=0.05$.

RESULTS AND DISCUSSION

Multiple linear regression analysis using $M(1)$, $M(2)$, and the CEC values obtained via the buffered $BaCl_2$ method ($CEC_{8.1,I=0.3}$), showed that $R(1)_{8.1,I=0.3}$ equaled 0.0578 cmol(−) g^{-1} clay and $R(2)_{8.1,I=0.3}$ of organic C equaled 0.3214 cmol(−) g^{-1}. The standard error s.e. of the estimates were 0.006 and 0.057, respectively. The explained variance R^2 of the multiple linear regression equation was 0.82. The $R(1)_{8.1,I=0.3}$ value found is normal for soils containing mixtures of illites and smectites (6,21). The $R(2)_{8.1,I=0.3}$ is of the same order of magnitude as found by Addiscott (22) and Helling et al. (8). When it is assumed that organic C is 55 percent of organic matter, then the calculated charge of organic matter at pH 8.1 is 0.187 cmol(−) g^{-1}.

Figures 1a and b give estimates and standard error of difference (sed) found for $D(1)$ and $D(2)$ in Step 1, respectively. The pH_{act} ranged from 4.5 to 7.3. At pH_{act} values smaller than 5.5 clay content of the test soils was low and sed of $D(1)$ estimates were relatively large. When pH_{act} was larger than 6.5 sed values were small because then most test soils were loam and clay soils having a considerable clay content. In the pH range from 5.5 to 6.5 sand, loam as well as clay soil were present, resulting in intermediate sed values. The estimated $D(1)$ values did not differ significantly from zero (Fig. 1a). As a result, $D(1)$ does not depend on pH_{act} and $R(1)_{pH,I=0.03}$ equals $R(1)_{8.1,I=0.03}$. The absence of an effect of pH on $R(1)$ is often reported in literature (6). $D(2)$ was most times significantly higher than zero (Fig. 1b) which means that $D(2)_{pHact}$ was significantly different from zero. Figure 1b shows that the estimates of $D(2)$ are relatively high at pH values between 4.5 and 5.0 and between 6.0 and 6.5 indicating that $D(2)_{pHact}$ is not linear related to pH. Table 2 gives the statistical results of curve fitting the relationship between $D(2)$ and pH_{act} (Step 2).

In Step 3, the estimated value $R(1)_{8.1,I=0.03}$ equals 0.0447 cmol(−) g^{-1} clay (s.e.d.=0.0382) and $R(2)_{8.1,I=0.03}$ equals 0.3845 cmol(−) g^{-1} organic C (s.e.d=0.0159). The estimate $R(2)_{8.1,I=0.03}$ is not significantly different from $R(2)_{8.1,I=0.3}$ as estimated by multiple linear regression using the potential CEC values obtained via the buffered $BaCl_2$ method. The estimate of $R(1)_{8.1,I=0.03}$ agrees very well with the charge of illitic clay minerals, namely 0.040 cmol(−) g^{-1} clay (21), but this estimate is not significantly different from zero and considerably lower than $R(1)_{8.1,I=0.3}$ as estimated by multiple linear regression using

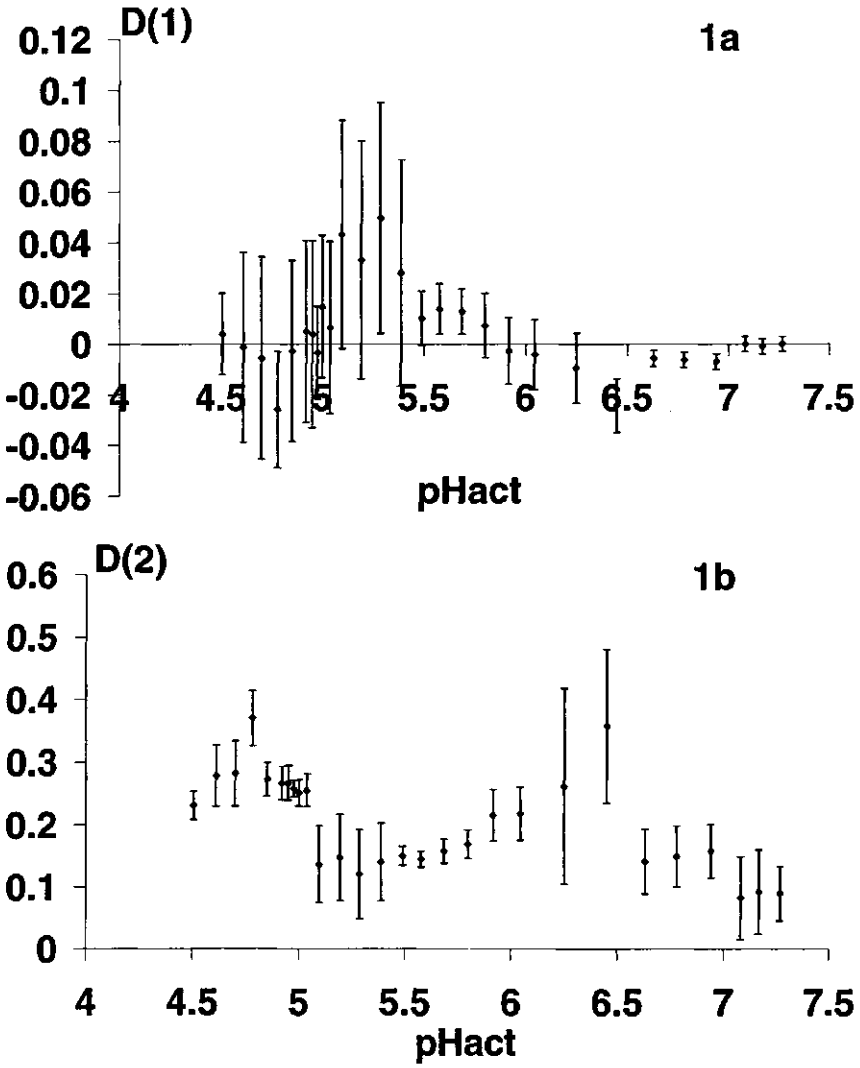

Figure 1. Estimated $D(1)$ and $D(2)$ values according to Step 1 (see Materials and Methods). Error bars equal to the standard error of difference of the estimates. $D(1)$ and $D(2)$ in cmol(−) g^{-1}.

CEC values obtained via the buffered $BaCl_2$ method. After a more precise analysis of the experimental data it turned out that one soil showed a leverage effect. When the statistical analysis was repeated without this soil, then $R(1)_{8.1,I=0.03}$ equals 0.0624 cmol(−) g^{-1} clay (s.e.d.=0.027) and $R(2)_{8.1,I=0.03}$ equals 0.295 cmol(−) g^{-1} organic C (s.e.d. = 0.0193). These results are in close agreement with and not significantly different from $R(1)_{8.1,I=0.3}$ and $R(2)_{8.1,I=0.3}$ as found by multiple linear regression.

Table 2. Statistical Results of Curve Fitting the Relationship Between $D(2)$ and pH_{act} in Step 2 [$D(2)_{pHact} = a+bx+cx^2+dx^3+ex^4+fx^6$; $x=pH_{act}$ and $R^2=0.80$]

Coefficient	Estimate	Standard Error
a	−1083.15	0.0390
b	909.5273	160.4117
c	−295.814	52.28245
d	45.23841	8.027384
e	−2.89521	0.5167
f	0.005491	0.000996

According to Equation (7), $R(2)_{pHact,I=0.03}$ equals the summation of $R(2)_{8.1,I=0.03}$ and $D(2)_{pHact}$ as found via curve fitting (Table 2). Filling in $R(2)_{pHact,I=0.03}$ in Equation (3) gives Equation (10).

$$CEC_{act} = [M(1) \times 0.062] + [M(2) \times (0.295 - D(2)_{pHact})] \quad (10)$$

Equation (10) is valid in the pH range from 4.5 to 7.3. Figure 2 gives the calculated relationship between pH_{act} and the negative charge $Q(2)$ of 10 g organic C kg^{-1} dry soil using Equation 10 when $M(1)$ is zero. The $Q(2)$ decreases in the pH range from 4.5 to 4.7, increases in the pH range from 4.7 to 5.5, decreases in the pH range from 5.5 to 6.3, and then increases again. This relationship differs from the normal positive (linear or curved) relationship between pH and $Q(2)$ often found for organic matter or organic C originating from a specific soil (8,23). In our study, the pH–$Q(2)$ relationship is deduced from and comprises the charge characteristics of organic C in six different soils with a comparable pH_{act} and therefore, the pH–$Q(2)$ relationship may differ from pH–$Q(2)$ relationships found for one type of organic C. In Figure 2 three zones can be distinguished. In the pH range from 4.7 to 5.5, $Q(2)$ increases when pH increases. In this range the test soils were most times acid sandy soils. In the pH range from pH 5.5 to 6.3 $Q(2)$ decreases when pH increases. In this range the test soils were sandy soils, loamy soils, and clay soils. In the pH range from pH 6.3 to pH 7.3 most test soils were clay soils and $Q(2)$ increases when pH increases. When it is assumed that the origin of organic C in the tested agricultural soils is the same, namely residues from crops and manures, then the course of $Q(2)$ may be explained by the effect of the interaction between organic matter and the surface of clay minerals on $R(2)$ (24). In the pH range lower than 5.5 the effect of this interaction on $R(2)$ will be small because clay content is very low. In clay soils, in the pH range higher than 6.3, the interaction may seriously affect $R(2)$. Organic C in the double layer of clay minerals will have different ionization characteristics because I and pH at the surface of

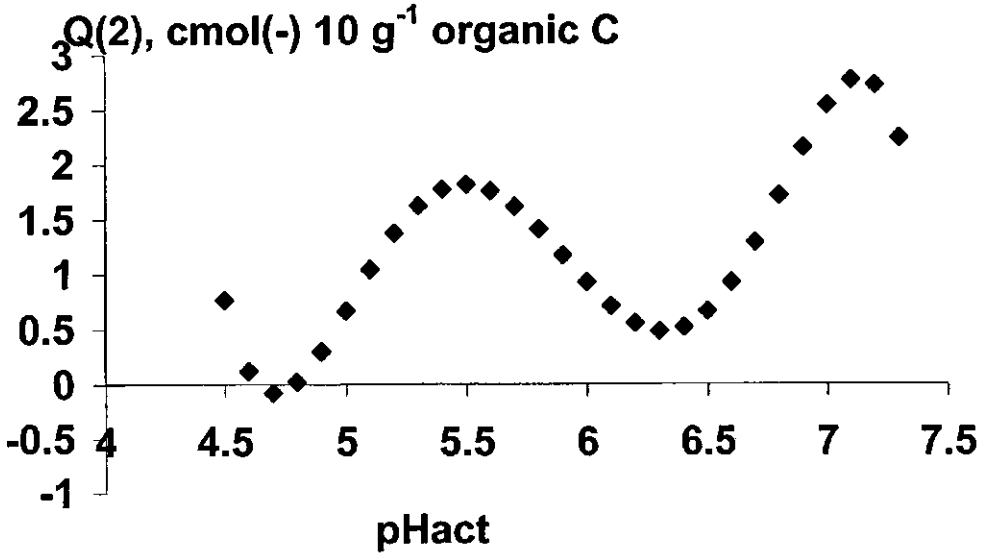

Figure 2. Relationship between pH_{act} and $Q(2)$.

clay minerals differ from that in solution. It is well known that pH at the clay surface can be 1 to 2 pH units lower than in the solution (6). If it is true that interaction plays a role, then $R(2)$ of organic C in a sandy soil with a pH A will be more or less equal to $R(2)$ of organic C in a clay soil having a pH between A+1 and A+2. It follows from Figure 2 that this relationship exist for sandy soils having a pH between pH 5 and pH 5.5 and clay soils between pH 6.3 and 6.8. In the pH range of 5.5 to 6.3, the effect of interaction of organic C and clay becomes more dominant when pH increases because the clay content of the soils increases.

Figure 3 gives the relationship between the measured CEC_{act} of the 39 test soils on the X-axis and the calculated CEC_{act}, CEC_{act}-calc, on the Y-axis. Moreover, the 1 : 1 relationship is given. CEC_{act}-calc was calculated using Equation (10) for the test soils in the pH range of 4.5 to 7.3. The relationship (R^2=0.88) could be described as: CEC_{act}-calc=1.50 (s.e.d.=2.96) + 0.823 (s.e.d=0.059)* CEC_{act}. The intercept was not significantly different from zero but the slope was significantly different from 1.

Figure 4 gives the relationship between the measured CEC_{act} and calculated CEC_{act}-calc for 38 different agricultural soils in the pH range of 4.5 to 7.3 using Equation (10). Since the organic matter content of the 38 soils was known and not organic C, it was assumed that organic C is 55% organic matter. Then, the statistical analysis showed that CEC_{act}-calc=−1.59 (s.e.d.=3.43) + 0.99 (s.e.d.=0.06)×CEC_{act} (R^2=0.89). The intercept was not significantly different from zero and the slope was not significantly different from 1. It is concluded that the tested procedure can be used for estimation of CEC_{act}. Moreover, Equation (3)

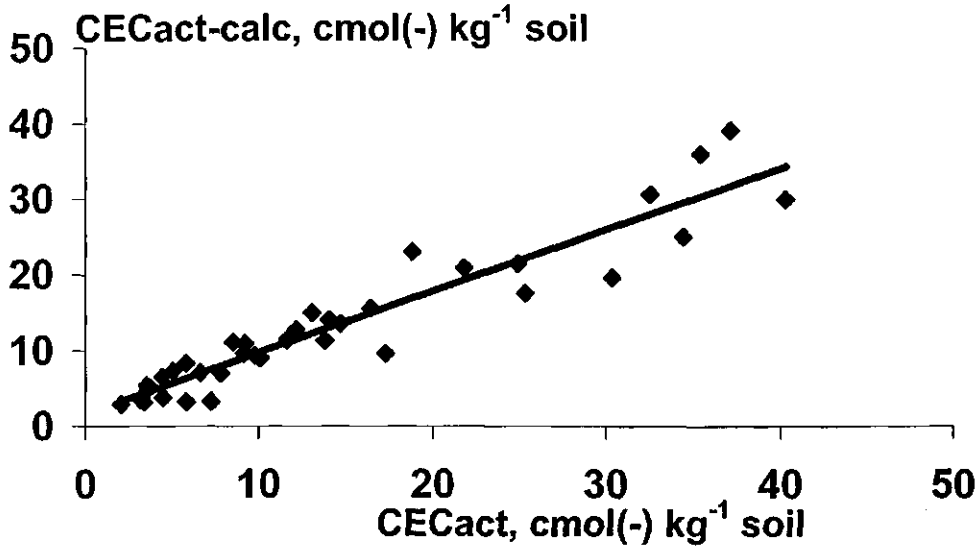

Figure 3. Relationship between measured CEC_{act} and calculated CEC_{act}, CEC_{act}-calc. Results from 39 test soils.

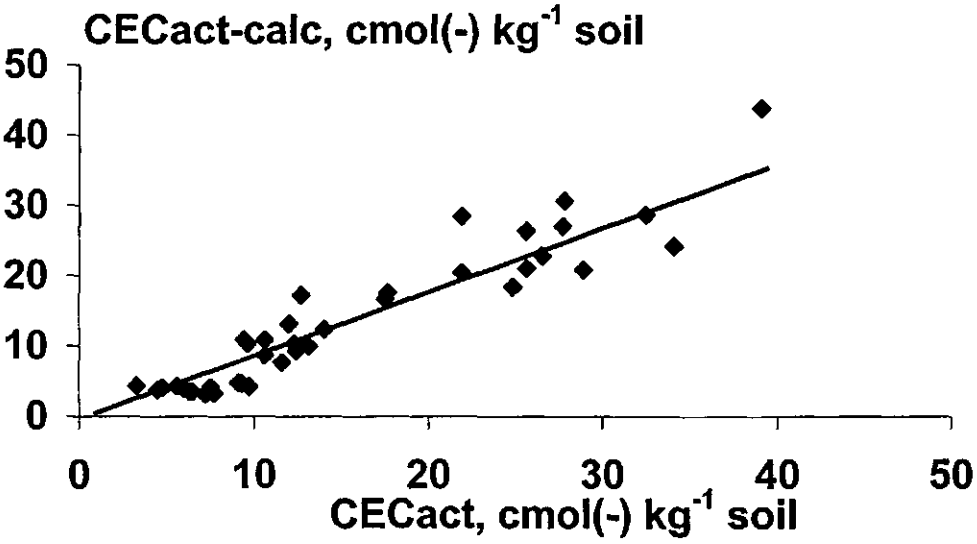

Figure 4. Relationship between measured CEC_{act} and calculated CEC_{act}, CEC_{act}-calc according to Equation (10). Results from 38 agricultural soils in The Netherlands.

will simplify the conversion of conventional soil testing programs for Mg into a 0.01 *M* $CaCl_2$ soil testing program.

CONCLUSIONS

This study showed that the actual CEC, CEC_{act}, of agricultural soils in The Netherlands can be estimated according CEC_{act}: $[M(1)\times 0.0624] + [M(2)\times(0.295 - D(2)_{pHact})]$.

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CHAPTER 7

THE 0.01 M $BACL_2$ SOIL EXTRACTION METHOD AS AN ESTIMATE OF THE POOL OF PLANT AVAILABLE POTASSIUM

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THE 0.01 M $BACL_2$ SOIL EXTRACTION METHOD AS AN ESTIMATE OF THE POOL OF PLANT AVAILABLE POTASSIUM

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ABSTRACT

The soil-plant-nutrient relationships in a four-quadrant scheme can be used for the set up of more fundamental fertilization schemes. The absence of a soil testing method determining the pool of plant available nutrient hinders the use of this scheme. Unbuffered 0.01 M $BaCl_2$ is an effective extractant for the determination of exchangeable cations like K, Mg, Ca, etc. When K extracted by 0.01 M $BaCl_2$ would equal the pool of plant available K in a soil, this would promote the use of the four-quadrant scheme and thus the design of a new K fertilization scheme. Goal of this study was to investigate the relationship between $BaCl_2$ extractable soil K (K-$BaCl_2$) and the pool of plant available soil K.

The double pot technique (DPT) and the test crops maize and tomato were used to determine the pool of plant available K of eight agricultural soils differing widely in K soil status and soil characteristics. Dry matter production of tomato and maize was highly correlated to K-$BaCl_2$ (R^2 >0.95). K-$BaCl_2$ equaled K uptake of maize and tomato at clay contents < 20 % but K uptake exceeded K-$BaCl_2$ at clay contents > 20%. We argue that clay minerals have released non-exchangeable K in these soils. It is therefore concluded that K-$BaCl_2$ is available for plant uptake and can be used as the lower boundary of the magnitude of the pool of plant available K. K-$BaCl_2$ equals the pool of plant available K in soils with not more than 20 % clay. For soils higher in clay our data suggest a release of 5 mg K per % clay, on average.

INTRODUCTION

The perspectives of 0.01 M $CaCl_2$ as a multi-nutrient soil extractant are challenging (Houba et al., 1986). However, the interpretation of $CaCl_2$ extraction data and the set up of fertilization schemes needs further study. Baier and Baierova (1998) have shown that 0.01 M $CaCl_2$ extractable K (K-$CaCl_2$) is related to K extracted by conventional K extractants. Therefore, it has been proposed to use these relationships to convert conventional fertilization schemes for K into a $CaCl_2$ fertilization scheme for K. It is widely known and well documented that plant growth and K uptake are related to the amount of soil exchangeable K (Bear et al., 1945; Bray, 1945; Pearson, 1952). Therefore, soil exchangeable K could be a basis for the set up of K fertilization schemes. $CaCl_2$ extractable K is generally lower than exchangeable K determined via the unbuffered 0.01 M $BaCl_2$ method (ISO 11260, 1994). The four-quadrant scheme (De Willigen and Van Noordwijk, 1987) comprises relevant soil-plant-nutrient relationships and can be used for the set up of more fundamental (and dynamic) fertilization schemes. In the four-quadrant scheme, the pool of plant available nutrient is an important soil nutrient availability index. At this moment no soil testing method is available for the determination of this pool. This hinders the use of this scheme for the set up of K fertilization schemes. The unbuffered 0.01 M $BaCl_2$ extraction procedure (ISO 11260, 1994) is a common soil extraction method for the determination of exchangeable cations. In the $BaCl_2$ procedure, soils are extracted three times by a 0.1 M $BaCl_2$ solution to replace exchangeable cations. Ba ions have a strong replacing power, are not preferentially adsorbed and do not cause collapse of phyllosilicates as do both K and NH_4 (Wada and Harada, 1969). Studies by Horn et al. (1982) and Gillman et al. (1983) have shown that extraction with Ba yields a comparable content of exchangeable bases as do procedures using NH_4 salts. Generally, K extracted by $BaCl_2$ is equal to or somewhat lower than K extracted by NH_4OAc (pH=7) (Gillman, 1979; Amacher et al., 1990; Simard and Zizka, 1994). In a previous study, a method has been proposed to estimate the amount of $BaCl_2$ extractable K (K-$BaCl_2$) from $CaCl_2$ soil extraction data (Van Erp et al., 2002). When it can be shown that K-$BaCl_2$ is plant available and equals the pool of plant available

K, then the combined use of the four-quadrant scheme and the $CaCl_2$ procedure may promote the set up of fundamental (and dynamic) K fertilization schemes.

Soil exhaustion via plant uptake is a direct method for the determination of the pool of plant available nutrients. Grezbisz and Oertli (1992, 1993) used a modified Neubauer test in which seedlings took up nutrients from a limited soil volume during a relatively short period of time (15-20 days). This method has the disadvantage that it is difficult to maintain an adequate status for the essential nutrients other than the nutrient under study. The double pot technique (Janssen, 1974; 1990) overcomes this problem. In the double pot technique (DPT), growing conditions and water and nutrient availability are optimal except for the nutrient under study. Uptake of this nutrient takes place from a limited volume of test soil. DPT can thus be regarded as a practical method of soil testing enabling the identification of nutrients in short supply without the use of chemical analysis. In DPT, the test soil will be very intensively rooted and soil moisture content is kept optimal. Therefore, plant nutrient uptake in DPT will equal or approach the pool of plant available soil nutrient. However, DPT is time consuming and labour intensive. Goal of this study was to study the relationship between 0.01 M $BaCl_2$ extractable soil K (K-$BaCl_2$) and the pool of plant available K using DPT.

MATERIALS AND METHODS.

The experiment has been carried out with eight test soils (Table 1). These soils include all combinations of a low, intermediate and high contents of K-$BaCl_2$ and 0.01 M $CaCl_2$ extractable K (K-$CaCl_2$). All test soils, except soil 7, have been chosen from a collection of 39 soils originating from the plough layer of agricultural soils in The Netherlands (Van Erp et al., 2001). K-$BaCl_2$ has been determined according to the unbuffered 0.01 M $BaCl_2$ extraction method (ISO 11260, 1994) and K-$CaCl_2$ according to the 0.01 M $CaCl_2$ method (Houba et al., 2000).

DPT was used to relate K-$BaCl_2$ of the test soils with K uptake and plant growth. The experimental set up of DPT consisted of a small upper pot (200 cm^3) standing on a larger lower pot (700 cm^3). The upper pot has a gauze bottom through which roots can grow. The upper pot was filled with moist (60 % of water holding capacity) test soil and then weighed. The lower pot was filled with nutrient solution containing all

TABLE 1. Characteristics of the eight test soils

Soil number	Soil type	Organic C, %	Clay, % < 2 µm	pH-$CaCl_2$	CEC, cmol(-) kg^{-1}	K-$CaCl_2$, mg kg^{-1}*	K-$BaCl_2$, mg kg^{-1}**
1	Sand	3.4	2	5.0	7.3	32	47
2	Loam	1.6	17	6.3	11.7	28	82
3	Clay	3	14	5.0	9.2	127	238
4	Clay	4.1	28	6.4	30.4	139	410
5	Sand	1	6	6.0	3.6	123	176
6	Clay	4.9	21	4.6	13.1	207	378
7	Clay	14	28	5.5	33.4	215	495
8	Loam	3.1	3	5.3	6.6	212	277

* = K extractable with 0.01 M $CaCl_2$; ** K extractable with 0.1 M $BaCl_2$.

essential nutrients except K (3mM $Ca(NO_3)_2$, 2 mM $NH_4H_2PO_4$, 0.75 mM $MgSO_4$, 0.5 mM $CaCl_2$, 1 mM NH_4NO_3, 0.5 mM $MgCl_2$, 1 ml l^{-1} of Hoagland's micro nutrient solution and 1 ml l^{-1} of Hoagland's Fe-EDTA solution). The test plants maize (Zea mays L.) and tomato (Solanum lycopersicum L.) were sown in the upper pot. When roots penetrated the gauze bottom they came in the nutrient solution of the lower pot. Test plants could take up K only from the test soil in the upper pot. The control treatment consisted of an upper pot filled with test soil 2 and a lower pot filled with the nutrient solution in which $CaCl_2$, NH_4NO_3 and $MgCl_2$ were replaced by 2mM KCl and 2 mM KNO_3. The total number of 'double pots' was 72 [(8 soil treatments + 1 control treatment) * 4 replicates * 2 test crops]. After filling the upper pots with moist soil, 3-4 seeds of the test crop were sown in each pot. The upper pots were then water sprayed and covered with plastic to ensure optimal germination conditions and placed upon the lower pot. The double pots were placed in a greenhouse on two tables, each containing 4 rows. Each row consisted of one test crop and one replicate of each treatment; i.e. 9 pots per row. Day/night temperature in the greenhouse was approx. 20/18°C. After germination, the number of seedlings was reduced to one plant per pot and illumination was provided (16 h day^{-1}; 84 J m^2s^{-1}). To maintain soil moisture content, the upper pots were weighed daily and water was added when necessary. To ensure comparable growing conditions for all pots both the rows and the position of the pots within the row were rotated daily. The solution in the lower pot was refreshed every three days.

Maize and tomato were harvested after 50 and 60 days, respectively. By that time, most treatments showed a very low growth rate. Fresh weight was determined for the shoots, and for the roots in the lower pot. The roots from the upper pot were washed with demineralised water in three replicates. The roots were dried in paper tissues and then fresh weight was determined. The soil of the upper pot of the fourth replicate was air-dried and used for determination of K-$BaCl_2$ after removing the air-dry root residues. The air-dry root residues were collected for determination of root dry matter production. Dry matter of all plant samples was determined after drying for two days at 70°C. Subsequently, the root and shoot material from one pot was mixed, ground and analyzed for K. The results were evaluated using analysis of variance and linear regression. Differences between treatments were tested according LSD test and Tukey's test at P=0.05 (Genstat 5 Committee, 1987).

RESULTS AND DISCUSSION

Total DM production of both tomato and maize grown on the control treatment with soil 2 was significantly higher than DM production of plants grown on soil 2 (Figure 1). This means that the presence of K in the lower pot promoted growth and DM production of the test crops compared to soil 2 were K was omitted in the lower pot. Evidently, the K status of soil 2 is too low for optimal DM production. In the beginning of the experiment, plant growth rate in the control treatment was low compared to e.g. soils 4 and 7 that both have a high K soil status. As soon as the roots in the control treatment penetrated the gauze bottom and came in contact with the nutrient solution in the lower pot, growth rate of the control treatment was comparable to that on soils 4 and 7. This means that the 'low' K soil status of soil 2 in the control treatment was responsible for the low growth rate just after germination.

TABLE 2. Mean dry weights of maize and tomato: D1= shoots, D2= roots upper pot, D3= roots lower pot, D4= total roots, and D5= total dry weight. Results in g per pot, average of 4 replicates. Results in the same column followed by the same letter are not significantly different (LSD test, P=0.05).

Soil	Maize					Tomato				
	D1	D2	D3	D4	D5	D1	D2	D3	D4	D5
1	3.00a	0.10a	0.14a	0.24a	3.24a	2.18a	0.08a	0.11a	0.19a	2.37a
2	4.12a	0.20a	0.24ab	0.48a	4.6a	2.86a	0.14ab	0.16ab	0.29a	3.08a
3	12.48b	1.12ab	0.88bc	2.00ab	14.48b	7.53b	0.47abc	0.57c	1.03bc	8.57b
4	28.56e	4.48d	2.90e	7.38e	35.94e	13.51c	0.89cd	0.99d	1.88de	15.39de
5	13.28b	1.48abc	0.98c	2.46b	15.74b	8.14b	0.33ab	0.49bc	0.82b	8.96bc
6	22.58d	2.90cd	1.78d	4.68cd	27.26cd	11.46bc	0.61bcd	0.85cd	1.46cd	12.91cde
7	22.92d	2.84cd	1.90d	4.74cd	27.46cd	14.72c	1.06d	1.12d	2.18e	16.90e
8	18.74c	2.08bc	1.66d	3.74bc	22.48c	11.22bc	0.63bcd	0.78cd	1.41cd	12.63bcd
Control	26.23de	3.98d	1.93d	5.90de	32.13de	23.66d	1.86e	1.81e	3.67f	27.33f

Table 2 presents the dry matter (DM) production of i) the shoots, ii) the roots in the upper pot, iii) the roots in the lower pot, iv) the roots in upper plus lower pot, and v) of the whole plant. Results of fresh yield were comparable to those of dry matter (not shown).

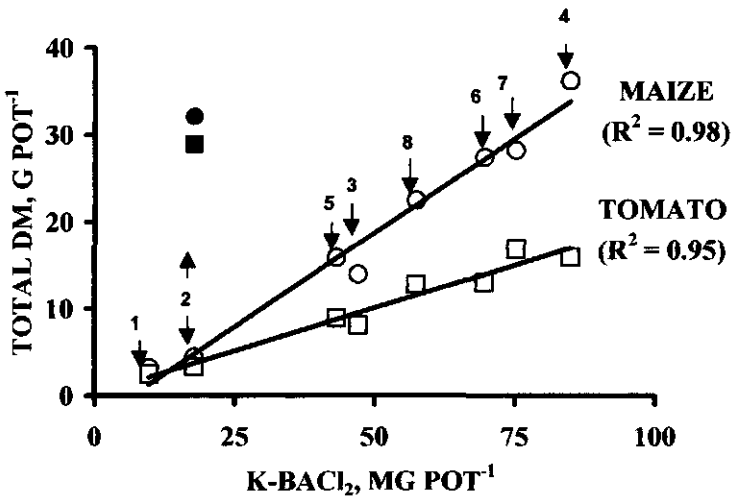

FIGURE 1. Relationship between $BaCl_2$ extractable K (K-$BaCl_2$) of the test soils and total dry matter production of tomato and maize; ●= maize control treatment, ■= tomato control treatment. Numbers in the figure indicate soil number.

Figure 1 shows the relationship between K-$BaCl_2$ and total DM production. The soil with the highest K-$BaCl_2$ content (soils 4, 6, 7) showed the highest DM production and the soil with the lowest K-$BaCl_2$ content (soils 1, 2) the lowest DM production. DM production of maize grown on soils 4, 6 and 7 was not significantly different from the control treatment. These three soils have a high K-$BaCl_2$ content suggesting that K was not limiting DM production in these soils. K-$CaCl_2$ showed a moderate relationship with total DM production of maize and tomato (results not shown). There was a good relationship ($R^2 > 0.95$) between K-$BaCl_2$ and DM production (Figure 1). Since all other growth factors were optimal in DPT, this means that K-$BaCl_2$ has determined the level of DM production of the test crops.

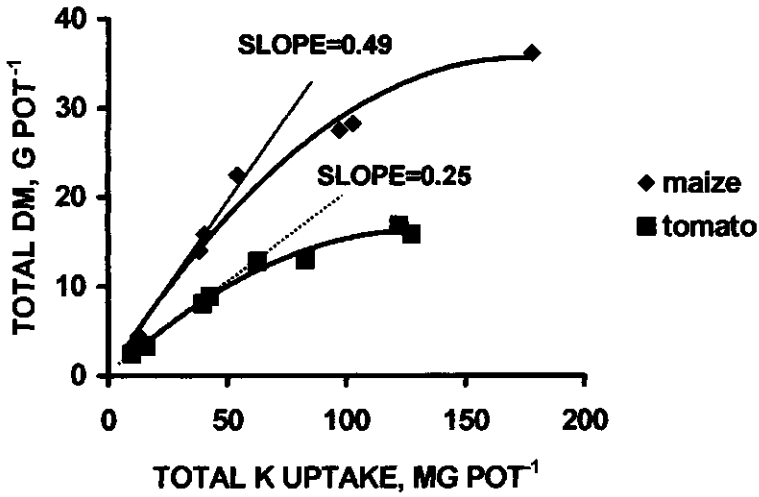

FIGURE 2. Relationship between K uptake and dry matter production of whole maize and tomato plants

The relationship between total K uptake and total DM production of tomato and maize is given in Figure 2. DM production of both maize and tomato increased proportionally with K uptake from 0 to about 50-60 mg K per pot and leveled off at higher rates. In the linear part of this relationship, K content of the whole plant was 0.49% for maize and 0.25% for tomato. Under these conditions, these figures may thus be considered as the critical concentrations for the respective species. The K content of the control plants was 1.66% for maize and 2.84 % for tomato.

The relationship between soil K-$BaCl_2$ content and total K uptake of the plants is presented in Figure 3. An almost 1:1 relationship was found between K-$BaCl_2$ and K uptake for five test soils suggesting that K-$BaCl_2$ equals the pool of plant available K in these soils. K-$BaCl_2$ content of all five soils was smaller than 60 mg pot $^{-1}$ (i.e. 300 mg kg $^{-1}$ soil).

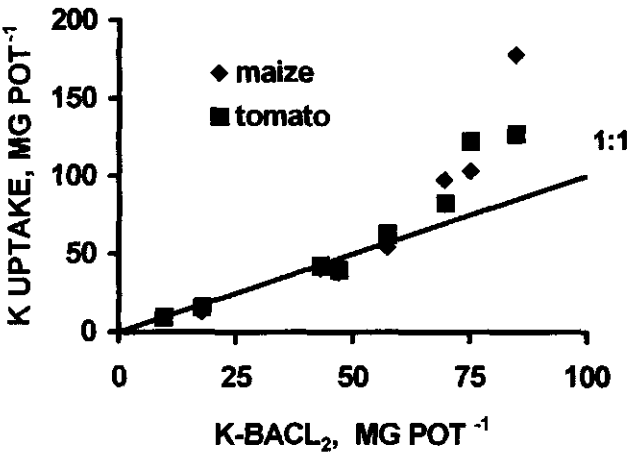

FIGURE 3. Relationship between $BaCl_2$ extractable K (K-$BaCl_2$) and K uptake of whole tomato and maize plants.

K uptake exceeded K-$BaCl_2$ in three clay soils with high K-$BaCl_2$ values. In these soils K-$BaCl_2$ does not equal the pool of plant available K. It is possible that in these clay soils 0.01 M $BaCl_2$ has underestimated exchangeable K content. In literature it is often found that e.g. NH_4OAc (pH=7) extractable soil K is somewhat higher than 0.1 M $BaCl_2$ extractable soil K (Gillman, 1979; Amacher et al., 1990; Simard and Zizka, 1994). The difference in extractable K would result from the chemical characteristics of NH_4 which are comparable to K. When a NH_4OAc solution is added to a clay soil, NH_4 may replace K from specific binding sites at the clay minerals. Ba added via 0.1 M $BaCl_2$ cannot replace K from such sites. However, differences in K extracted between NH_4OAc (pH=7) and 0.1 M $BaCl_2$ are generally much smaller than the difference we found between K plant uptake and K-$BaCl_2$ in this DPT experiment. It is postulated here that in the DPT experiment plant roots have taken up non-exchangeable soil K from illitic clay minerals (Mengel and Uhlenbecker, 1993) which are common in agricultural soils in The Netherlands. These clay minerals may have high affinity sites for K in the wedge shaped voids of their mineral lattice (Mc Lean and Watson, 1985). When the concentration of K in the soil solution decreases during crop growth, the bonding energy of K to the high affinity sites is overcome and K will

desorb (Mc Lean and Watson, 1985). In DPT, the rooting density is very high and conditions are optimal for plant growth. Since K uptake on the three clay soils exceeds K-$BaCl_2$ content, it is likely that the soil solution has been K depleted followed by a release of non-exchangeable K from the clay minerals.

The K-release from clay minerals can be estimated from a balance-sheet approach. In this case, K-release was calculated as the summation of K-$BaCl_2$ of the soils at harvest and total K plant uptake minus the initial K-$BaCl_2$ content of the soils. Figure 4 clearly show that the calculated K-release was negligible in the range from 0 to about 20 % clay. K release increased considerably when clay content increased from 20% to 30%. The available data suggests that in the pots about 5 mg K was released per % clay, on average.

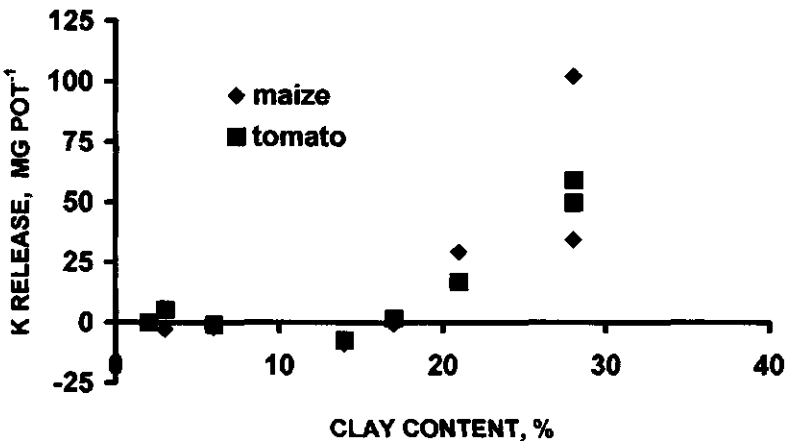

FIGURE 4. Relationship between clay content and calculated K release, per pot.

It is concluded that 0.01 M $BaCl_2$ extractable K is strongly correlated to dry matter production of maize and tomato. On soils containing less than 20 % clay, K-$BaCl_2$ equals the total K uptake of maize and tomato. In these soils K-$BaCl_2$ is an indicator of the pool of plant available K. In soils with more than 20 % clay, we assume that non-

exchangeable K in clay minerals becomes plant available. For these soils K-$BaCl_2$ is the lower boundary of the pool of plant available K in soil.

The use of K-$BaCl_2$ in the four-quadrant scheme as an indicator of the pool of plant available K seems adequate on soils containing less than 20 % clay. Since determination of K-$BaCl_2$ requires an extra analytical procedure in soil testing, estimation of the magnitude of K-$BaCl_2$ using the multi-nutrient $CaCl_2$ procedure (Van Erp et al., 2002) seems promising. For soils containing more than 20 % clay detailed research into the working mechanisms of unbuffered $BaCl_2$ extraction will be necessary to determine its applicability for the determination of the pool of plant available K.

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CHAPTER 8

EXCHANGE SELECTIVITY OF CA, MG AND K IN SOILS DURING THE 0.01 M $CaCl_2$ EXTRACTION PROCEDURE

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EXCHANGE SELECTIVITY OF CA, MG AND K IN SOILS DURING THE 0.01 M $CaCl_2$ EXTRACTION PROCEDURE.

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ABSTRACT

After the 0.01 M $CaCl_2$ soil extraction procedure considerable amounts of exchangeable K and Mg are retained at the soil exchange sites. This may underestimate the soil supply of K and Mg. In this paper a method has been derived to calculate the amount of Mg and K retained at the exchange sites after extraction. Aim of this study was i) to determine $K_{Ca\rightarrow Mg}$, $K_{Ca\rightarrow K}$ and $K_{Mg\rightarrow K}$, the selectivity coefficients of the Ca-Mg, Ca-K and Mg-K exchange reactions during the 0.01 M $CaCl_2$ procedure, and ii) to identify soil characteristics and factors contributing to the variation in these selectivity coefficients.

Twenty-eight agricultural soils from The Netherlands were chosen with Ca, Mg and K as dominant exchangeable cations. Both water extractable and exchangeable Ca, Mg and K were determined as well as general soil characteristics. $K_{Ca\rightarrow Mg}$ ranged from 0.70 to 1.26 (av. 0.87) and decreased when % organic C increased. $K_{Ca\rightarrow K}$ ranged from 3.35 to 17.02 (av. 8.35) and was correlated with the ratio of Ca and K concentration in the filtrate after extraction, the fraction of the total negative charge originating from clay, and with clay content. $K_{Mg\rightarrow K}$ ranged from 4.38 to 17.39 (av. 9.48) and was positively correlated with the fraction of the total negative charge originating from clay. $K_{Mg\rightarrow K}$ and $K_{Ca\rightarrow K}$ were highly correlated.

The selectivity coefficients were used to calculate the amount of soil exchangeable Ca, Mg of K and their relative saturation of the exchange sites after $CaCl_2$ extraction. There was a good agreement between measured and calculated saturation of the soil exchange sites with K and Mg for most soils. We conclude that $K_{Ca\rightarrow Mg}$, $K_{Ca\rightarrow K}$ and $K_{Mg\rightarrow K}$ selectivity

coefficients and the proposed method for calculation of residual cations are applicable for neutral, non-sodic soils.

INTRODUCTION

The use of 0.01 M $CaCl_2$ as a multi-nutrient soil extractant has been proposed by Houba et al. (1986). Several studies have shown that ions extracted with $CaCl_2$ are well related to those extracted by conventional procedures (Baier and Baierova, 1998; Fotyma et al., 1998; Loch et al., 1998). It has been proposed to use these relationships to convert fertilizer recommendation schemes based on conventional procedures into $CaCl_2$ fertilizer recommendations schemes (Houba et al., 1986; Fotyma et al., 1998; Van Erp et al., 2001b). The amount of $CaCl_2$ extractable nutrient element can be related to soil nutrient supply under field conditions, because of comparable pH and ionic strength.

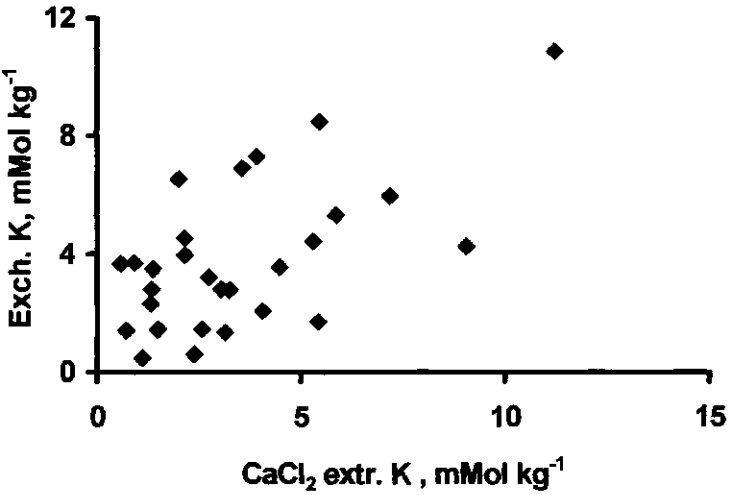

FIGURE 1. $CaCl_2$ extractable K and the amount of exchangeable K remaining at the soil exchange sites after the 0.01 M $CaCl_2$ extraction. Results from 39 agricultural soils.

Ion concentrations in the filtrate after the $CaCl_2$ extraction are the resultant of chemical processes that redistribute nutrient elements over the liquid and solid phase. Figure 1 shows that a considerable amount of K remains at the exchange sites of the solid phase after extraction. We found that on clay soils 20-50% of exchangeable K is extracted and 50-80

% on sand soils (Van Erp et al., 1998). When the $CaCl_2$ procedure is repeated, more of this exchangeable K can be released (Van Erp et al., 1998).

It is well documented that plant growth and K and Mg uptake are related to exchangeable concentrations (Bear et al., 1945; Bray, 1945; Pearson, 1952; Rice and Kamprath, 1968). The 0.01 M $CaCl_2$ procedure does not extract all exchangeable Mg and K and may therefore underestimate the actual supply of Mg and K. It is postulated here that the agricultural interpretation of the amount of $CaCl_2$ extractable K and Mg will improve, when the amount of exchangeable K and Mg retained at the exchange sites can be taken into account.

The amount of a cation that retains at the exchange sites equals the multiplication of the relative charge fractions of that cation at the exchange sites and the total charge of these sites, divided by the charge of the cation. The total charge of the sites equal the actual CEC and the charge of the cation equals its valency. At equilibrium, the relative cationic composition can be calculated from the cationic composition of the liquid phase and the selectivity coefficients of the prevailing cation exchange reactions. The concentration of cations in the liquid phase after $CaCl_2$ extraction can be measured. However, there is no insight into the selectivity coefficients of exchange reactions during the $CaCl_2$ extraction.

Aim of this study is to determine $K_{Ca\rightarrow Mg}$, $K_{Ca\rightarrow K}$ and $K_{Mg\rightarrow K}$, the selectivity coefficients of the Ca-Mg, Ca-K and Mg-K exchange reactions during the 0.01 M $CaCl_2$ procedure.

EXCHANGE CHEMISTRY

In the $CaCl_2$ procedure, pH and nutrient element concentration in the liquid phase of the soil suspension are in (adsorption) equilibrium state after a 2 h extraction period (Van Erp et al., 1998). Then, the distribution of cations over the liquid phase and the soil exchange sites obey the Gaines & Thomas approach for cation exchange reactions (Gaines and Thomas, 1953). The Gaines &Thomas approach (1953) is thermodynamically sound and is applicable to multi-cationic systems (Bolt, 1979). Equation 1 gives the mathematical description of a binair cation exchange reaction according to Gaines & Thomas.

$$K_{XaA->XbB} = \frac{(E_B)^{1/b} * (A)^{1/a}}{(E_A)^{1/a} * (B)^{1/b}} \quad (1)$$

In Equation 1, E_A and E_B are the dimensionless charge fractions of cation A and B, respectively, at the soil exchange sites X. (A) and (B) represent the activity of A and B in the liquid phase of the soil suspension in mol l^{-1}. $K_{XaA \rightarrow XbB}$ is the selectivity coefficient for the exchange reaction in which A at X is replaced for B. The valence of A and B is represented by a and b, respectively. The selectivity coefficient is an indicator of the preference of X for cation A as compared to cation B. In Equation 1, (A) can be substituted by:

$$f_A * \frac{L_A}{VOL} \quad (2)$$

in which f_A is the dimensionless activity coefficient of A, VOL the total volume of the liquid phase in l kg^{-1} soil and L_A the total amount of A in the liquid phase in mol kg^{-1} soil. L_A equals the multiplication of VOL and [A]. [A] is the concentration of A in mol l^{-1}.
Further, E_A in Equation 1 can be substituted by:

$$\frac{(T_A - L_A) * a}{Z} \quad (3)$$

in which Z represents the total negative charge of X in mol(-) kg^{-1} soil, and T_A is the total amount of cation A at X and in the liquid phase, in mol kg^{-1} soil. Then, T_A-L_A represents the amount of cation A at X in mol kg^{-1} soil. Equations 2 and 3 can also be worked out for cation B. Substitution of (2) and (3) in Equation 1 gives Equation 4.

$$K_{X_aA \rightarrow X_bB} = \frac{(\frac{(T_B - L_B)*b}{Z})^{1/b} * (\frac{f_A * L_A}{VOL})^{1/a}}{(\frac{(T_A - L_A)*a}{Z})^{1/a} * (\frac{f_B * L_B}{VOL})^{1/b}} \quad (4)$$

When $K_{XaA \rightarrow XbB}$, f_B, f_A, a, b, Z, VOL, L_A and L_B are known for a binary system, then T_A and T_B can be deduced. For that, Equation 4 can be mathematically solved, taking into account that $E_A + E_B = 1$ (see Equation 5).

$$\frac{(T_A - L_A)*a}{Z} + \frac{(T_B - L_B)*b}{Z} = E_A + E_B = 1 \quad (5)$$

The Gaines & Thomas approach also applies to ternary systems in which the cations A, B and C exchange at X (Bolt, 1979). Then, Equation 4 describes the exchange reaction in which A at X is replaced by B. The selectivity coefficient for the exchange reaction in which A at X is replaced by C, $K_{XaA \rightarrow XcC}$, can be derived comparable to $K_{XaA \rightarrow XbB}$ using equations 1 to 3. T_A, T_B and T_C can then be deduced when $K_{XaA \rightarrow XbB}$, $K_{XaA \rightarrow XcC}$, f_A, f_B, f_c, a, b, c, Z, VOL, L_A, L_B and L_C are known. For that, the equations of $K_{XaA \rightarrow XbB}$ and $K_{XaA \rightarrow XcC}$ (see Equation 4) can be mathematically solved, taking into account that $E_A + E_B + E_C = 1$.

In non-sodic, non-acidic agricultural soils Ca, Mg and K are the major exchangeable cations. When these soils are extracted according to the $CaCl_2$ procedure and when adsorption equilibrium is attained after 2 h, then the soil suspension can be treated as a ternary system which obeys the Gaines & Thomas approach. Equation 1-5 should apply to this system and the amount of Ca, Mg and K at X and in the liquid phase, T_A, T_B and T_C, respectively, can be calculated as described above. The necessary variables a, b, c, VOL, L_A, L_B and L_C are known or can be calculated from the $CaCl_2$ extraction results. Z, which equals the actual CEC of the soil, can be estimated when pH-$CaCl_2$, organic C and clay content are known (Van Erp et al., 2001a). The activity coefficients f_A, f_B, f_C are unknown. However, f_A, f_B, f_C are constant since the ionic strength (I) of the soil suspension during $CaCl_2$ extraction is largely determined by the ionic strength of the 0.01 M $CaCl_2$ solution (I=0.03). Because of their constancy, f_A, f_B, f_C can easily be incorporated into $K_{XaA \rightarrow XbB}$

and $K_{XaA \rightarrow XcC}$. In Equation 6 this is worked out for $K_{XaA \rightarrow XbB}$.

$$K_{A \rightarrow B} = K_{X_aA \rightarrow X_bB} * \frac{(f_B)^{1/b}}{(f_A)^{1/a}} = \frac{(\frac{(T_B - L_B) * b}{Z})^{1/b} * (\frac{L_A}{VOL})^{1/a}}{(\frac{(T_A - L_A) * a}{Z})^{1/a} * (\frac{L_B}{VOL})^{1/b}} \quad (6)$$

The magnitude of $K_{A \rightarrow B}$ and $K_{A \rightarrow C}$ is unknown and not measured before. At this moment, this hinders the applicability of the derived method for estimating T_A, T_B and T_C in ternary soil systems during the $CaCl_2$ procedure. It is therefore not possible to calculate the amount of A, B and C remaining at X, T_A-L_A, T_B-L_B and T_C-L_C, respectively, in which we are highly interested.

A study has been carried out to:

- deduce the $K_{Ca \rightarrow Mg}$, $K_{Ca \rightarrow K}$ and $K_{Mg \rightarrow K}$ selectivity coefficients of the Ca-Mg, Ca-K and Mg-K exchange reactions during the 0.01 M $CaCl_2$ procedure and,
- to identify soil characteristics and factors contributing to the variation in these selectivity coefficients.

MATERIALS AND METHODS

Thirty-nine soil samples with widely differing soil characteristics were collected from the plough layer of agricultural fields in The Netherlands. After sampling, the soil samples have been pretreated according to ISO 11464 (1994). Subsequently, the soils have been extracted according to the unbuffered 0.01 M $BaCl_2$ method (ISO 11260, 1994) to determine the actual CEC and the exchangeable Ca, Mg, K, Al, NH_4 and Na concentrations. Extractable Na and NH_4 were negligible in all soils. Soils were discarded in the further study when the amount of exchangeable Al was more than 1 % of the actual CEC. This was done to ensure that only ternary soil systems with Ca, Mg and K were involved. After this selection 28 soils remained. Organic C content (ISO 14235, 1998), clay content (NEN 5753, 1994), pH KCl (ISO 10390, 1994) and pH $CaCl_2$ (Houba et al. 2000) were determined (Table 1).

TABLE 1. Relevant soil characteristics of the 28 test soils.

Characteristic	Average	Minimum	Maximum
Organic C, %	2.91	0.6	8.3
Clay, %	19	3	52
pH-$CaCl_2$	6.22	4.32	7.68
pH-KCl	6.06	4.13	7.46
Actual CEC , cmol(-) kg^{-1} (1)	18.8	2.66	50.42
% Organic C/ % clay	0.268	0.037	1.033
Ca, cmol(+) kg^{-1} (2)	17.35	2.54	48.7
Mg, cmol(+) kg^{-1} (2)	1.85	0.17	4.07
K, cmol(+) kg^{-1} (2)	0.74	0.16	2.20

(1) Calculated, see materials and methods. (2) Determined via the unbuffered 0.01 M $BaCl_2$ method (ISO 11260, 1994)

Equation 5 has been used to calculate $K_{Ca\rightarrow Mg}$, $K_{Ca\rightarrow K}$ and $K_{Mg\rightarrow K}$. The variables T_{Mg} and T_K were considered to be represented by Mg and K extracted by unbuffered $BaCl_2$ (ISO 11260, 1994). T_{Ca} equaled the sum of Ca extracted by unbuffered $BaCl_2$ and Ca added to the soil via the 0.01 M $CaCl_2$ extractant. L_{Ca}, L_{Mg} and L_k were calculated from VOL of the 0.01 M $CaCl_2$ procedure and [Ca], [Mg] and [K] in the filtrate after the $CaCl_2$ extraction. Because unbuffered $BaCl_2$ (ISO 11260, 1994) turned out to underestimate the actual CEC (Van Erp et al., 2002), Z was calculated in this study as the total charge of 0.1 M $BaCl_2$ extractable Ca, Mg and K plus the charge of Ca added via 0.01 M $CaCl_2$ minus the charge of 0.01 M $CaCl_2$ extractable Ca, Mg and K. It was assumed that no cationic complexes were present or adsorbed.

Via regression analysis the magnitude of the calculated selectivity coefficients has been related to soil characteristics (pH-KCl, pH-$CaCl_2$, % organic C, % clay), the ratio % organic C/% clay (Curtin et al. 1998), F_{clay}, $[Ca]^{½}/[K]$, $[Ca]^{½}/[Mg]^{½}$ and $[Mg]^{½}/[K]$. F_{clay} is the fraction of Z originating from clay particles. The charge of clay particles is thereby set at 0.624 mol(-) kg^{-1} (Van Erp et al., 2001a). $[Ca]^{½}/[K]$, $[Ca]^{½}/[Mg]^{½}$, $[Mg]^{½}/[K]$ are indicators of the cationic composition of the filtrate and calculated using [Ca], [Mg] and [K]. Statistical analyses were carried out using the statistical package Genstat 5 (Genstat 5 Committee, 1987).

RESULTS AND DISCUSSION

Table 1 gives a summary of the characteristics of the 28 test soils.

In one sand soil, F_{clay} exceeded 1 which means that the estimated total negative charge of the clay particles exceeded Z. A possible explanation for this is that the assumed charge of clay particles, i.e. 0.624 mol(-) kg^{-1}, is too high for the type of clay particles present in this sandy soil. Therefore, the sand soil was omitted from the study and 27 test soils resulted.

$K_{Ca \rightarrow Mg}$

Table 2 gives an overview of the selectivity coefficients. $K_{Ca \rightarrow Mg}$ of the exchange reaction in which Ca at X is replaced for Mg ranged from 0.70 to 1.26 with an average value of 0.87 and a standard error of 0.02. $K_{Ca \rightarrow Mg}$ values in this range are often found for soils as well as for specific soil constituents (e.g. Bruggenwert and Kamphorst, 1979).

TABLE 2. $K_{Ca \rightarrow Mg}$, $K_{Ca \rightarrow K}$ and $K_{Mg \rightarrow K}$ selectivity coefficients

Parameter	Selectivity coefficients		
	$K_{Ca \rightarrow Mg}$	$K_{Ca \rightarrow K}$	$K_{Mg \rightarrow K}$
Average	0.87	8.35	9.48
Standard deviation	0.11	3.49	3.41
Standard error	0.02	0.67	0.66
Median	0.85	7.33	8.91
Minimum value	0.70	3.35	4.38
Maximum value	1.26	17.02	17.38

Ca and Mg are bivalent and have a comparable hydrated ion radius. When the exchange sites X show no preference for Ca or Mg, i.e. standard free enthalpy (ΔG^0_{ex}) equals 0, then $K_{Ca \rightarrow Mg}$ should be 1 (Bolt, 1979). In 26 soils $K_{Ca \rightarrow Mg}$ was smaller than 1 which means that exchange sites in natural soils generally prefer Ca to Mg. One soil had a selectivity coefficient of 1.26 indicating a preference for Mg to Ca. An overestimation of $K_{Ca \rightarrow Mg}$ cannot be excluded for this soil since the absolute values of Z and L_{Mg} are (very) low and therefore an analytical error cannot be excluded.

When F_{clay} ranges from 0.2 to 0.3, i.e. the clay exchange sites have a minor contribution to

Z, then $K_{Ca\rightarrow Mg}$ ranges from 0.7 to 0.8. $K_{Ca\rightarrow Mg}$ approaches 1 when F_{clay} ranges from 0.9 to 1. A lack of preference at these high F_{clay} values suggests that Ca and Mg are electrostatically bound at the clay surfaces. When F_{clay} is low, exchange sites on organic matter are the main contributors to Z. Then, small $K_{Ca\rightarrow Mg}$ values suggest that exchange sites on organic matter prefer Ca to Mg. In literature, it is often found that organic matter prefers Ca to Mg because of the formation of specific organic complexes (Salmon, 1964; Hunsaker and Pratt, 1971; Murray and Linder, 1984; Baes and Bloom, 1988). Figure 2 confirms that organic matter, represented by % organic C, is related to the magnitude of $K_{Ca\rightarrow Mg}$. $K_{Ca\rightarrow Mg}$ decreases from 1.25 to 0.9 in the range from 0% to 2% organic C. In the range from 2% to 8% organic C $K_{Ca\rightarrow Mg}$ decreases gradually from 0.9 to 0.8.

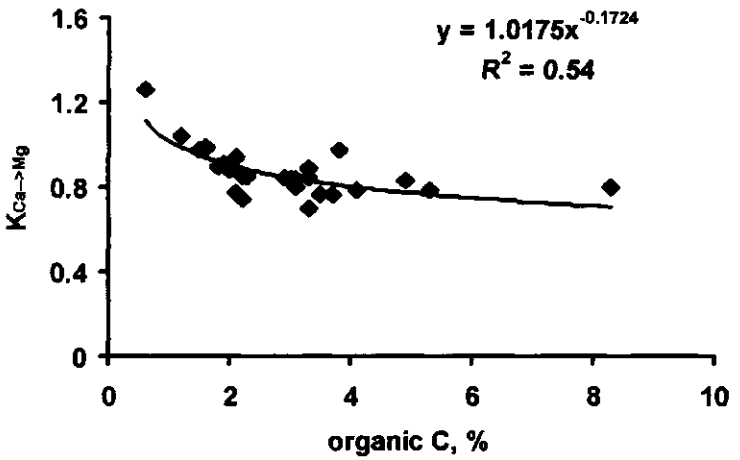

FIGURE 2. The relationship between % organic C and the calculated $K_{Ca\rightarrow Mg}$ of 27 test soils

According to literature, there is no clear effect of pH on Ca-Mg selectivity. No effect of pH on Ca-Mg selectivity was found for smectite dominated soils (Curtin et al., 1998), pure smectite (Clark, 1966) and montmorillonite soils in the pH-range 6-7 (Fletcher et al., 1984 a,b). Edmeades and Judd (1980) found that liming of New Zealand soils generally increased selectivity for Ca relative to Mg. Our experimental data showed no effect of pH-

$CaCl_2$ or pH-KCl on $K_{Ca\rightarrow Mg}$. Curtin et al., (1998) found that the ratio %organic matter/%clay was the best single indicator of Ca-Mg selectivity. In our study the ratio % organic C/% clay was not related to $K_{Ca\rightarrow Mg}$.

$K_{Ca\rightarrow K}$

$K_{Ca\rightarrow K}$ of the exchange reaction in which Ca at X is replaced for K ranged from 3.35 to 17.02 with an average value of 8.35 and a standard error of 0.67. F_{clay} showed a moderate, positive relationship with $K_{Ca\rightarrow K}$ (R^2=0.33). This means that soil exchange sites show a preference for K when clay minerals are the main contributors to Z. $K_{Ca\rightarrow K}$ should be 1.65 when exchange sites show no preference for Ca or K, i.e. standard free enthalpy (ΔG^0_{ex}) equals 0 (Bolt, 1979). Exchange sites prefer the divalent cation Ca to the monovalent cation K when these cations are electrostatically bound. As a result $K_{Ca\rightarrow K}$ is smaller than 1.65. This is often found for Ca-K exchange on e.g. montmorillonite clay minerals (Bruggenwert and Kamphorst, 1979). Illitic clay minerals show a broad range of $K_{Ca\rightarrow K}$ values which are most times (much) larger than 1.65. The different types of exchange sites on illitic clay minerals are probably responsible for this (Bolt et al., 1963). On the planar exchange sites cations are electrostatically bound and Ca is preferred over K. The edge-interlayer sites and interlattice sites show a high affinity for K and as a result K is highly preferred over Ca. Especially, the interlattice sites show a high preference for K leading to very high $K_{Ca\rightarrow K}$ selectivity coefficients (Bolt et al., 1963; Ehlers et al., 1967).

In The Netherlands, the clay fraction is most times dominated by illitic type of clay minerals. Therefore, the clay soils with high F_{clay} and Z values will probably contain many affinity sites of illitic clay minerals. As a result $K_{Ca\rightarrow K}$ is much higher than 1.65. In literature it is often found that $K_{Ca\rightarrow K}$ is much higher than 1.65 for real soils (Bruggenwert and Kamphorst, 1979).

$[Ca]^{½}/[K]$ of the filtrate after $CaCl_2$ extraction showed a positive relationship with $K_{Ca\rightarrow K}$ (Figure 3). Since, [Ca] in the filtrate is "constant" and about 0.01 M., the preference of the soil exchange sites for K increases when [K] decreases.

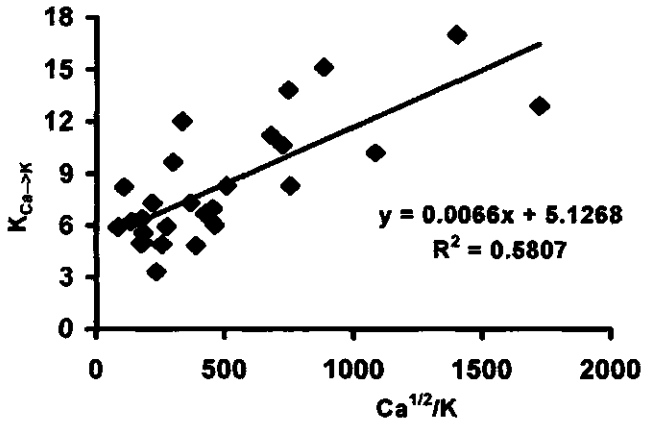

FIGURE 3. Relationship between $[Ca]^{½}/[K]$ and the $K_{Ca\rightarrow K}$ selectivity coefficient of the 27 soils.

Differences between the measured and estimated $K_{Ca\rightarrow K}$ values in Figure 3 were related to F_{clay} and % clay. Multiple linear regression analysis showed that $K_{Ca\rightarrow K}$ can be estimated according Equation 7.

$$K_{Ca\rightarrow K} = 2.26 + (0.007 * [Ca]^{½}/[K]) + (7.526 * F_{clay}) - (0.101 * \% \text{ clay}) \quad (R^2 = 0.85) \qquad (7)$$

In literature, an effect has been suggested of pH on Ca-K selectivity in organic matter containing soils and variable charge soils (Munns, 1976; Curtin et al., 1995; Rhue and Mansell, 1988). A pH increase would promote the development of exchange sites that prefer Ca. Our experimental data did not show such effect of pH on $K_{Ca\rightarrow K}$.

$K_{Mg\rightarrow K}$

$K_{Mg\rightarrow K}$ of the exchange reaction in which Mg at X is replaced for K ranged from 4.38 to 17.38 with an average value of 9.48 and a standard error of 0.66. $K_{Mg\rightarrow K}$ values exceeded 1.65, which means that the soil exchange sites prefer K (Bolt, 1979). $K_{Mg\rightarrow K}$ was not related to %organic C, %clay, pH, $[Mg]^{½}/[K]$ and the ratio % organic C/% clay. There was a moderate positive relationship between F_{clay} and $K_{Mg\rightarrow K}$ (Figure 4). Illitic clay minerals in the soil clay fraction and their high affinity sites for K may explain the increase in $K_{Mg\rightarrow K}$

when F_{clay} increase. Deviations of the regression line were not related to other (soil) characteristics.

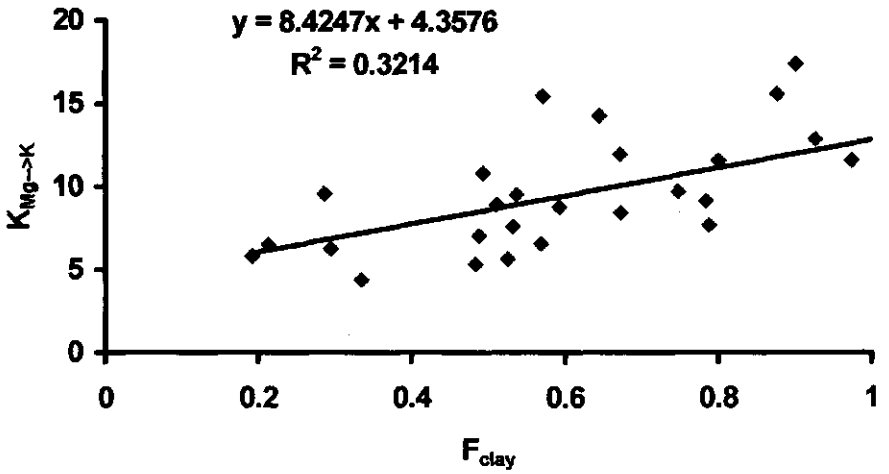

FIGURE 4. Relationship between F_{clay} and $K_{Mg \rightarrow K}$.

EVALUATION

After extraction of the 27 test soils according to the $CaCl_2$ procedure, the occupation of Z with Ca ranged from 87% to 97.8%, for Mg from 0.5% to 7.7% and for K from 0.7% to 7.2%. When Z is 40 cmol(-)kg^{-1}, one percent occupation with Ca, Mg and K would equal 280 kg Ca ha^{-1}, 168 kg Mg ha^{-1} and 560 kg K ha^{-1} assuming a plough layer weight of 3.5 million kg. These calculations show that the amount of K and Mg not extracted by the $CaCl_2$ procedure is considerable when it is expressed on a hectare basis. Residual K and Mg may exceed the average annual plant uptake of K and Mg.

In this study $K_{Ca \rightarrow Mg}$, $K_{Ca \rightarrow K}$ and $K_{Mg \rightarrow K}$ selectivity coefficients have been derived for exchange processes during the 0.01 M $CaCl_2$ extraction procedure. $K_{Ca \rightarrow K}$ is related to $[Ca]^{½}/[K]$, F_{clay} and % clay (Equation 7), $K_{Ca \rightarrow Mg}$ to % organic C (Equation 8), and $K_{Mg \rightarrow K}$ to F_{clay} (Equation 9).

$$K_{Ca\rightarrow Mg} = 1.0175 * (\%organicC)^{-0.1724} \qquad (R^2 = 0.54) \qquad (8)$$

$$K_{Mg\rightarrow K} = 4.3576 + 8.4247 * F_{clay} \qquad (R^2 = 0.32) \qquad (9)$$

Equations 7, 8 and 9 can be used for an arbitrary soil to obtain estimates for the selectivity coefficients. $K_{Mg\rightarrow K}$ shows a moderate relationship with F_{clay} and therefore the estimates of $K_{Mg\rightarrow K}$ may be unreliable.

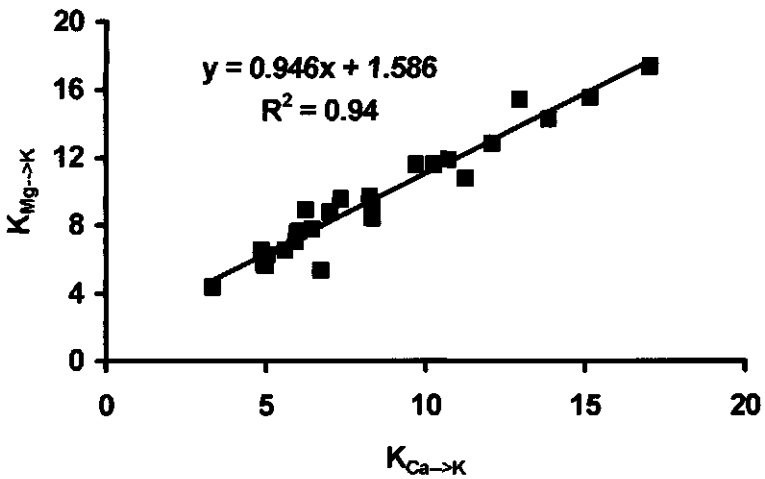

FIGURE 5. Relationship between $K_{Mg\rightarrow K}$ and $K_{Ca\rightarrow K}$ for the 27 test soils.

Figure 5 shows that a very good relationship exists between $K_{Mg\rightarrow K}$ and $K_{Ca\rightarrow K}$ found for the test soils in this study. This relationship can be used for estimation of $K_{Mg\rightarrow K}$ when $K_{Ca\rightarrow K}$ is known.

According to the method proposed in this paper, the total amounts of Ca, Mg and K at X and in the liquid phase (T_{Ca}, T_{Mg} and T_K) has been calculated. In these calculations $K_{Ca\rightarrow Mg}$ and $K_{Ca\rightarrow K}$ have been derived from Equations 7 and 8. Subsequently, the amount of Ca, Mg and K remaining at X after the $CaCl_2$ extraction (T_{Ca}-L_{Ca}, T_{Mg}-L_{Mg}, T_K-L_K) has been calculated.

Figure 6 gives the relationship between the measured %Mg at Z and the difference between the estimated %Mg and measured %Mg, Δ % Mg, at Z for the 27 soils. For 26 soils, Δ % Mg ranged between –1% and 1%. For K all soils deviated less than 2% and 24 soils deviated less than 1%. For Ca it was found that 22 out of 27 soils deviate less than 1% but all soils deviated less than 2% percent. It is concluded that for most soils the estimated % occupation of Z with K and Mg equals the measured % occupation +/- 1%.

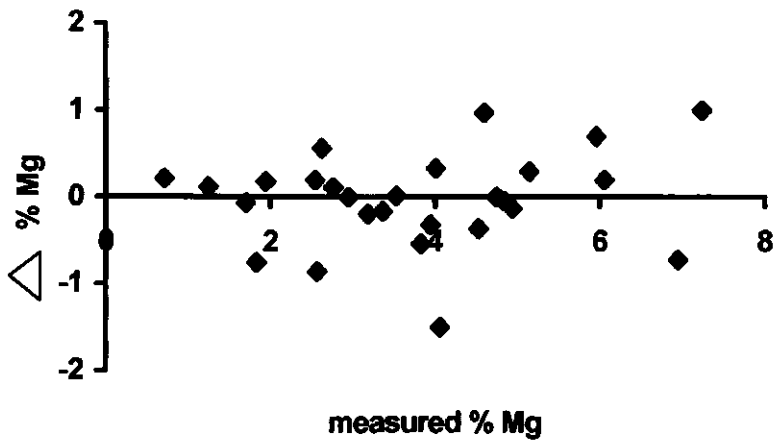

FIGURE 6. Relationship between the measured % Mg at the exchange sites Z and the difference between the estimated and measured % Mg (Δ %Mg).

During the $CaCl_2$ procedure the ionic strength, *I* equals 0.03 M and the activity coefficients, e.g. f_A, f_B, f_C are constant. Because of their constancy, the activity coefficients were incorporated in $K_{Ca\rightarrow Mg}$, $K_{Ca\rightarrow K}$ and $K_{Mg\rightarrow K}$ (Equation 6). In sodic soils or just after fertilization *I* may be higher than 0.03 M. The magnitude of the "constant" f_A, f_B, f_C and with that the selectivity coefficients will then change accordingly. The selectivity coefficients derived in this study are therefore only applicable for exchange processes during the $CaCl_2$ procedure at I=0.03 M.

In this paper a method is described to calculate T_{Ca}, T_{Mg} and T_K for soils where Ca, Mg and

K are the dominant cations (ternary soil system). However, soils may contain (considerable) amounts of other cationic species, e.g. NH_4, Na or Al. For these multi-cationic soils the described method is also valid but the mathematical solution of the equations is much more complicated.

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CHAPTER 9

DETERMINATION OF CATION EXCHANGE CAPACITY AND BASE SATURATION USING BARIUM CHLORIDE SOLUTION: COMMENTS ON ISO PROCEDURE 11260

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DETERMINATION OF CATION EXCHANGE CAPACITY AND BASE SATURATION USING BARIUM CHLORIDE SOLUTION; COMMENTS ON ISO PROCEDURE 11260.

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ABSTRACT

The total charge of the individual cations extracted according to the unbuffered $BaCl_2$ method (ISO 11260) often exceeds the charge of the actual CEC determined in the same procedure. A study has been carried out to determine the backgrounds for this difference. Twenty-eight soils have been used with Ca, Mg and K as the dominant exchangeable cations. The soils have been extracted with unbuffered and buffered $BaCl_2$, KCl and water. The total charge of water extractable cations could explain only part of the observed difference. In soils with CEC values > 25 cmol(-) kg^{-1}, the measured actual CEC was considerably higher when the amount of soil weighed out was 50 percent of the amount recommended in ISO 11260. This result means that the replacing power of the added $MgSO_4$ is not sufficient to exchange Ba from all soil exchange sites resulting in an underestimation of the actual CEC in the ISO procedure. In soils with pH higher than 5.5-6.0, the unbuffered $BaCl_2$ method replaces exchangeable Ca (specifically) bound to organic matter where the KCl method cannot. This Ca exchange is not complete when ionic strength is larger than 0.75 M. We conclude that the difference between the total (positive) charge of cations replaced by 0.1 M $BaCl_2$ and the total (negative) charge of the actual CEC, results from i) the cations present in the original soil suspension or released from readily soluble minerals, and ii) an underestimation of the actual CEC in soils high in CEC when extracted according ISO 11260 (1994).

INTRODUCTION

In 1986, Houba et al. proposed the use of 0.01 M $CaCl_2$ as a multi-nutrient soil extractant. The perspectives for the development of a multi-nutrient $CaCl_2$ soil testing program are good (Van Erp et al., 1998). One of the aims of our $CaCl_2$ research program is to deduce selectivity coefficients of cation exchange reactions at soil exchange sites during the $CaCl_2$ procedure. For the derivation of these selectivity coefficients, the total charge of the exchange sites during extraction (= actual CEC) as well as type and amount of exchangeable cations should be known (Van Erp et al., 2002). Moreover, the charge balance must be closed, i.e. the measured total charge of exchangeable cations should equal the measured charge of the actual CEC plus dissolved cations. The unbuffered 0.01 M $BaCl_2$ method may be a helpful extraction method since it determines the (actual) CEC as well as the amount of exchangeable cations in a single analytical procedure.

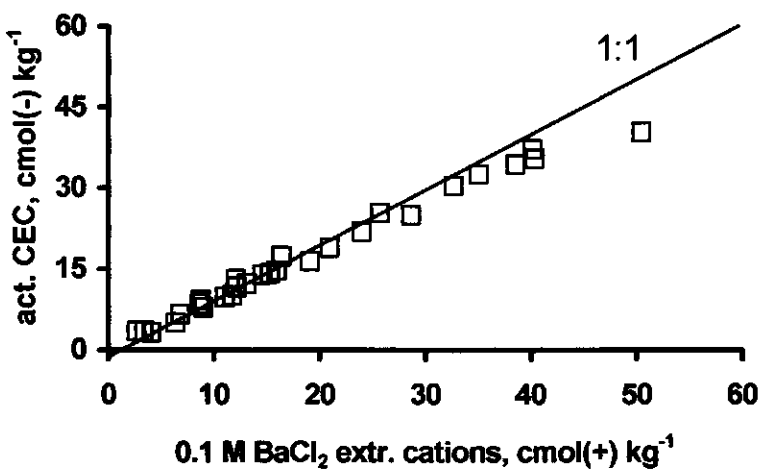

FIGURE 1. Relationship between the total charge of $BaCl_2$ extractable Ca, Mg and K, in cmol(+) kg^{-1}, and the total charge of the actual CEC measured according to the unbuffered $BaCl_2$ method in cmol(-) kg^{-1} (ISO 11260,1994).

In Figure 1 there is a tendency that the total (positive) charge of $BaCl_2$ extractable Ca, Mg and K exceeds the (negative) charge of the actual CEC determined via ISO 11260.

Deviations increased at higher actual CEC. A higher content of dissolved cationic species seems unlikely because all soils originate from the top layer of agricultural soils after a period of nutrient depletion by crops.

The unbuffered 0.01 M $BaCl_2$ according to ISO 11260 (1994) integrates the original $BaCl_2$ method (Gillmann, 1979,1981,1987) with modifications proposed by Hendershot and Duquette (1986). In ISO 11260 (1994), a 0.1 M $BaCl_2$ solution is added to the soil and then shaken for 1 h to replace the exchangeable cations with Ba. This step is repeated three times. The supernatant of all three batches is collected and the type and the amount of cations extracted is determined. Thereafter, the soil is equilibrated with 0.01 M $BaCl_2$ solution so that the ionic strength (I) and pH of the soil suspension is more or less equal to the actual pH and I of the soil under field conditions. Subsequently, a well-known amount of Mg is added to the soil suspension via a 0.02 M $MgSO_4$ solution. This addition results in the replacement of Ba for Mg followed by precipitation of the highly insoluble $BaSO_4$. The amount of Mg redrawn from the liquid phase is then used as an indicator of the actual CEC. There are many reports about the problem that more cations are extracted by 0.1 M $BaCl_2$ than the actual CEC permits. Possible explanations are a high content of dissolved cationic species in the soil solution and dissolution of readily soluble salts and soil carbonates. Deller (1983) concluded that the dissolution of carbonates cannot be responsible for the cation excess. There are also suggestions that during the 0.1 M $BaCl_2$ extraction Ba precipitates as $BaCO_3$ thereby dissolving $CaCO_3$, or that Ba exchanges with Ca and Mg at the surface of carbonates. However, Kuderna and Blum (1992) could not confirm this. They found that the excess of 0.1 M $BaCl_2$ extractable cations was related to the organic matter content of the soils. An underestimation of the actual CEC as explanation of the cation excess is thusfar mosttimes excluded, because the precipitation of $BaSO_4$ is expected to result in a complete exchange of Ba for Mg at the exchange sites (Sumner and Miller, 1996).

Figure 1 shows that the negative charge of the actual CEC is not equal to the total charge of the cations extracted by the unbuffered $BaCl_2$ method (ISO 11260, 1994). A study has been carried out to investigate the difference found.

MATERIALS AND METHODS

Twenty-eight soils have been collected from the top layer of agricultural soils in The Netherlands and pretreated according to ISO 11464 (1994). The pH-KCl of the soils was measured according to ISO 10390 (1994), organic carbon according to ISO 14235 (1998), the actual CEC and the amount of exchangeable Ca, Mg, K, Al, Na and NH_4 according to the unbuffered $BaCl_2$ method (ISO 11260, 1994) and exchangeable Ca and Mg according to the buffered $BaCl_2$ method (ISO 13536, 1995), and the 1 M KCl method (Mazaeva, 1967). Water extractable Ca, Mg and K was measured according to the 0.01 M $CaCl_2$ procedure (Houba et al., 2000) in which 0.01 M $CaCl_2$ has been replaced by demineralized water. In each of the soils Ca, Mg and K were the major exchangeable cations and exchangeable Al was <1 % of the actual CEC. Exchangeable Na and NH_4 were negligible in these soils. All statistical analyses were executed according to standard (multiple) linear regression analysis using the statistical package Genstat (Genstat 5 Committee, 1987).

RESULTS AND DISCUSSION

We define EXC as the difference between the total (positive) charge of 0.1 M $BaCl_2$ extractable Ca, Mg and K and the total (negative) charge of the actual CEC. Figure 2 shows that EXC exceeded the total charge of water extractable Ca, Mg and K (WSOL). When water extracts all cationic species in the original soil solution plus cations present in readily soluble salts, then $BaCl_2$ extracts extra cations. A possible source of the extra cations are (Ca and Mg) carbonates that dissolve during the $BaCl_2$ treatment.

The dissolution (rate) of carbonates during the $BaCl_2$ extraction is still not clear. From studies of Plummer et al. (1978) and Busenberg and Plummer (1982) it follows that i) the dissolution rate of carbonates is related to the square root of the proton activity, ii) the dissolution rate is low at pH 8 but increases at lower pH values, and iii) carbonate dissolution increases when contact time and surface area of the carbonate particles increases. Since, the pH drop after addition of 0.1 M $BaCl_2$ to a carbonate containing soil is relatively small (0.1-0.3 pH units), the contact time is only 3 times 1 h, and

because the surface area of the soil carbonates in the test soils was small (carbonates were visible by eye), it is reasonable to assume that the dissolution of soil carbonates during 0.1 M $BaCl_2$ extraction will be minimal. The experimental results of Deller (1983) and Kuderna and Blum (1992) confirm this assumption.

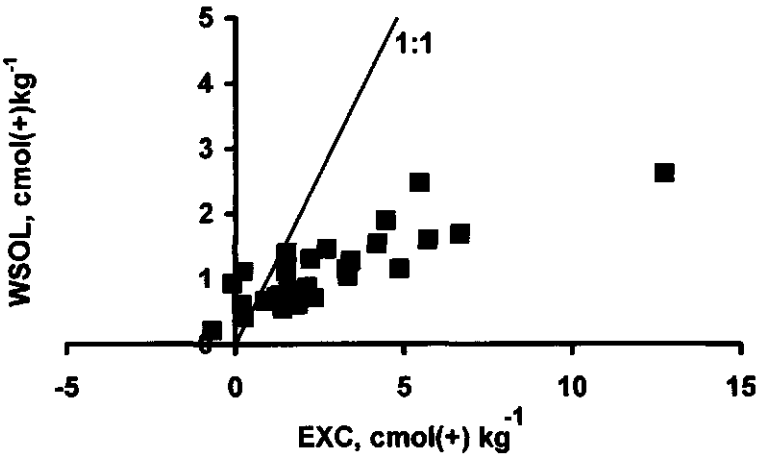

FIGURE 2. The relationship between EXC (the total (positive) charge of 0.1 M $BaCl_2$ extractable Ca, Mg and K minus the (negative) charge of the actual CEC) and WSOL, the total (positive) charge of water soluble Ca, Mg and K.

At pH 8.1 the dissolution of carbonates is negligible. Ca and Mg extracted according to the $BaCl_2$ method buffered at pH 8.1 should therefore equal Ca and Mg extracted according to the unbuffered $BaCl_2$ method, when soil carbonates do not dissolve. Figure 3 shows that Ca and Mg extracted by buffered $BaCl_2$ is smaller than with unbuffered $BaCl_2$. This can indicate that soil carbonates dissolve during the unbuffered $BaCl_2$ method. However, this phenomenon holds for both calcareous and non-calcareous soils; the dissolution of carbonates is therefore no explanation for the difference in Ca and Mg extracted between both $BaCl_2$ methods. Moreover, the difference in Ca and Mg extracted between both methods is large for soils having a pH higher than 7 (data not presented). It is unlikely that a relatively small pH increase from

an original soil pH higher than 7.0 to pH 8.1 results in such large reduction in extractable Ca and Mg. The results suggests that (an)other soil process(es) affect the difference in Ca and Mg extracted between both $BaCl_2$ methods.

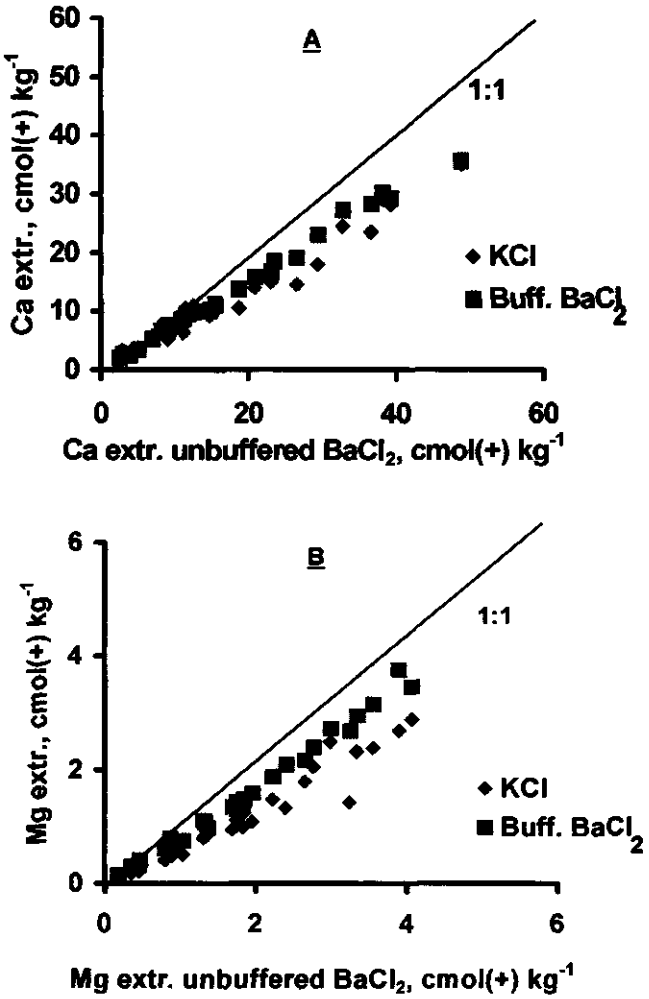

FIGURE 3. Relationship between calcium (A), and magnesium (B) extracted via the unbuffered $BaCl_2$ method (X-axis) and the amount of Ca and Mg extracted via the buffered $BaCl_2$ and 1 M KCl method (Y-axis).

Ca and Mg extracted via the KCl method is much lower than Ca and Mg extracted via the unbuffered $BaCl_2$ (Figure 3), suggesting that KCl and unbuffered $BaCl_2$ seem to extract Ca and Mg from different binding sites

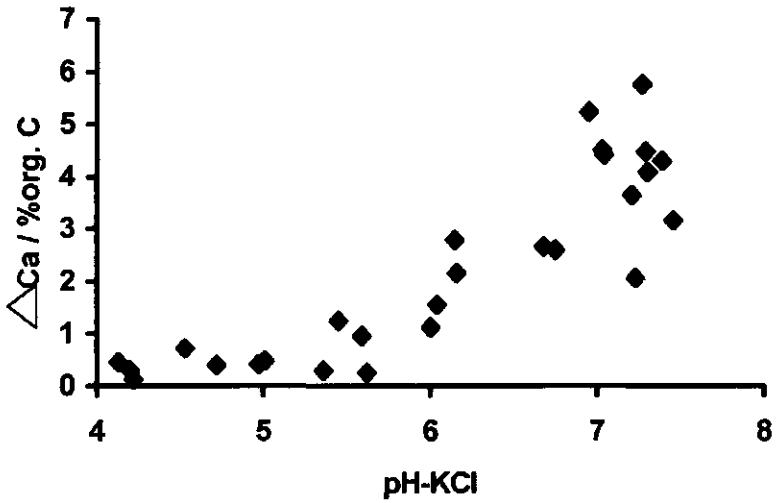

FIGURE 4. Relationship between pH KCl of the test soils and the difference in Ca extracted via the unbuffered $BaCl_2$ method and the KCl method expressed per % organic C (=Δ Ca/% org.C).

Figure 4 shows the relationship between pH KCl of the 28 test soils and the difference in Ca extracted via the unbuffered $BaCl_2$ method and the KCl method expressed per % organic C. PH KCl is used as an indicator of the pH of the soil suspension during the 1 M KCl extraction as well as the 0.1 M $BaCl_2$ extraction. In the pH range from 4 to 5.5 the ratio ranges from 0 to 1 and seems to be pH-independent. In the pH range from 5.5 to 7.5 the ratio increases when pH increases. This positive correlation may be interpreted as follows. Given a constant pH, the $BaCl_2$ method extracts much more Ca compared to the KCl method when % soil organic C increases. Given a constant soil organic C content, this increase means that the $BaCl_2$ method extracts much more Ca compared to the KCl method when pH increases. Monovalent cations like K show almost no specific interaction with bindings sites on organic matter. This in contrast to divalent cations (Murray and Linder, 1984; Baes and Bloom, 1988a; Baes and Bloom,

1988b; Van den Hoop et al., 1990). Therefore, the divalent cation Ba may extract more cations from binding sites at organic matter than the monovalent cation K. Moreover, it is well known that organic C shows an increased affinity for Ca when pH increases (De Wit et al., 1992; Milne et al., 1995). This increased adsorption is attributed to the increased dissociation of functional groups on organic matter leading to more negative charge (De Wit et al., 1993). Apparently, 0.1 M $BaCl_2$ is able to extract Ca and Mg from organic matter that could not be extracted with KCl.

Ca extracted by unbuffered $BaCl_2$ exceeded that extracted by the buffered $BaCl_2$ method (Figure 3A). It is unlikely that the Ba concentration is limiting the exchange process because the Ba concentration in the buffered $BaCl_2$ method is higher than in the unbuffered method, 0.1 and 0.5 M $BaCl_2$ respectively. As mentioned before, differences in Ca and Mg extracted between the two methods were large in (calcareous) soils with a high pH. In these soils, the pH during extraction is almost the same for the buffered and unbuffered method. Therefore, an effect of pH on the affinity of organic matter for Ca (and Mg) in these (calcareous) soils is unlikely. A significant difference between both $BaCl_2$ methods is that the unbuffered method extract soils at I=0.3 M (0.1 M $BaCl_2$ solution) and the buffered $BaCl_2$ method at I=1.5 M (0.5 M $BaCl_2$ solution). It is well known that I may affect the conformation and charge characteristics of organic matter (De Wit et al., 1992; Tits, 1990) as well as the affinity of organic matter for Ba, Ca and Mg (Baes and Bloom, 1988a, 1988b; De Wit et al., 1993). Our results suggest that at I=1.5 M the exchange of Ca by Ba is not complete. Baes and Bloom (1988a) found that three times washing of organic matter with 0.25 M $BaCl_2$ replaced all adsorbed Ca. We therefore suggest that at I larger than 0.75 M the replacement of Ca by Ba is repressed.

The CEC determination according to ISO 11260 will underestimate the actual CEC when soil particles are lost during the procedure or when the added $MgSO_4$ does not remove all adsorbed Ba. During the unbuffered $BaCl_2$ extraction the ionic strength of the soil suspension ranges from 0.03–0.3 M. In this range clay and organic matter coagulate and deposit. Therefore, losses of soil particles are assumed to be small.

An additional experiment has been carried out to check the sufficiency of the amount of $MgSO_4$ added according to ISO 11260 (1994) to replace all Ba adsorbed at the

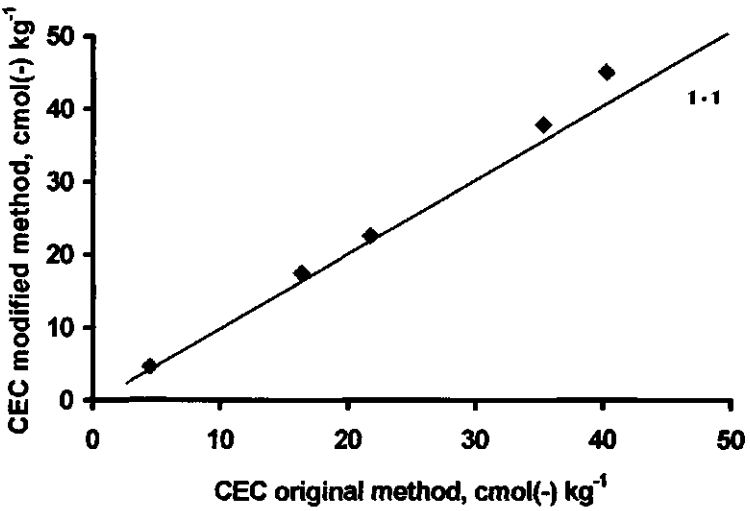

FIGURE 5. Relationship between the actual CEC measured according ISO 11260 using 3 g of test soil and a modified ISO method using 1.5 g of soil.

actual CEC. Instead of 3 g of soil 1.5 g soil was used. Figure 5 shows that the actual CEC measured according to the modified method exceeds the actual CEC measured according to the original method. Differences were small for soils having a low CEC but on soils having a CEC of about 35 and 40 cmol(-) kg^{-1} deviations were considerable. This result clearly indicates that added MgSO4 is not sufficient to replace all Ba at the actual CEC. Hendershot and Duquette (1986) suggested to repeat the procedure when more than 50 % of the added $MgSO_4$ was consumed. Then, the ionic strength *I* is kept in the desired range and the probability for incomplete exchange is minimized. In the ISO 11260 procedure, the $BaCl_2$ procedure is repeated when the actual CEC exceeds 40 cmol(-) kg^{-1} soil. This is remarkable since the total charge of the Mg added via $MgSO_4$, equals 40 cmol(+) kg^{-1}. The result is that in soils high in CEC a shortage of Mg (and SO_4) occurs. An incomplete Ba exchange and an underestimation of the actual CEC will then be the result

Equation 1 gives the linear regression equation of the relationship between the actual CEC measured by the original and modified method (see Figure 5).

$$\text{Modified } CEC_{act} = 1.1159 * \text{original } CEC_{act} - 0.8416 \ (r^2 = 0.99) \quad (1)$$

Figure 6 gives the relationship between the modified actual CEC of the 28 test soils, calculated according to Equation 1, and the amount of 0.1 M $BaCl_2$ extractable Ca, Mg and K minus the total charge of water extractable Ca, Mg and K, yielding an almost 1:1 relationship. This shows that the total charge of 0.1 M $BaCl_2$ extractable cations diminished with the charge of water extractable cations equals the total charge of the actual CEC. It is concluded that the present ISO 11260 underestimates the actual CEC of soils with a high CEC. ISO 11260 should therefore be adjusted.

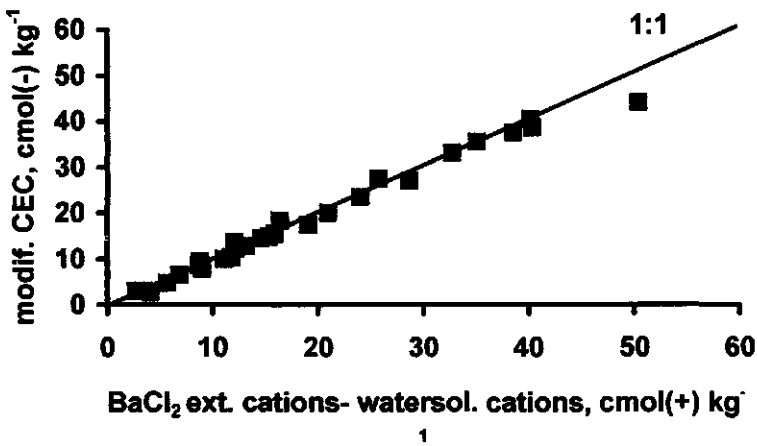

FIGURE 6. The relationship between the modified CEC, calculated according Equation 1, and the total charge of 0.1 M $BaCl_2$ extractable Ca, Mg and K minus the charge of water-extractable Ca, Mg and K.

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CHAPTER 10

TOWARDS MECHANISTIC RELATIONSHIPS BETWEEN SOIL NUTRIENT STATUS AND CROP GROWTH: SYNTHESIS AND CONCLUSIONS

TOWARDS MECHANISTIC RELATIONSHIPS BETWEEN SOIL NUTRIENT STATUS AND CROP GROWTH: SYNTHESIS AND CONCLUSIONS.

10.1 Multi-nutrient extractants

10.1.1 General

Most current soil testing programs are single nutrient programs (e.g. Soil and Plant Analysis Council Inc., 2000). When all essential nutrients have to be determined, numerous procedures need to be executed for sampling, sample preparation, extraction and analysis. As a consequence the use of these programs is time consuming and expensive.

Recent developments in analytical procedures, analytical techniques (e.g. inductively coupled plasma emission) and analytical equipment (e.g. autoanalyzer) have made simultaneous determination of several elements possible (Benton Jones, 1998). These developments have promoted the use and development of multi-nutrient extractants (Table 1). Multi-nutrient extractants are attractive from a laboratory point of view: soil sample treatment and soil sample extraction is executed only once and the subsequent simultaneous determination of nutrients ensures that soil testing data becomes available rapidly. Multi-nutrient extractions are cost-effective and thus will reduce soil testing costs for farmers. The use of the multi-nutrient extractants is often restricted to certain soil types (Table 1). The $CaCl_2$ method and the ion-exchange resins/membranes are applicable to all soil types. The chemical composition of the extracting reagent is often complex and in many cases pH and ionic strength of the soil suspension during extraction deviate strongly from average field conditions. As discussed in Chapter 3, the $CaCl_2$ reagent is an exception; 0.01 M $CaCl_2$ extracts nutrients at a pH and ionic strength comparable to average field conditions. The number of nutrients determined in the liquid phase after extraction varies from 6 for Mehlich No. 1 to 21 for $CaCl_2$. The analytical procedures and analytical techniques for the determination of the 21 nutrients in the $CaCl_2$ method have been described in detail (Houba et al., 2000). The repeatability and reproducibility of the $CaCl_2$ method is often better than for common (multi-nutrient) extraction methods (Houba et al., 1998)

TABLE 1. Some current multi-nutrient extraction methods, their applicability to soil types, the extracting reagent and the elements or nutrients determined (Benton Jones, 1998)

Method	Soil type	Extracting reagent	Elements or nutrients determined
Morgan	All acid soils and soil-less mixtures	0.54 M HOAc + 0.7 M NaOAc at pH 4.8	P, K, Ca, Mg, Cu, Fe, Mn, Zn, NO_3, NH_4, SO_4, Al, As, Hg, Pb
Wolf-Morgan	All acid soils and organic soils	0.0001 M DPTA +0.52 M HOAc + 0.073 M NaOAc at pH 4.8	P, K, Ca, Mg, Cu, Fe, Mn, Zn, Al, NO_3, NH_4
Mehlich No. 1	Acid sandy soils	0.05 M HCl + 0.0125 M H_2SO_4	P, K, Ca, Mg, Na, Mn, Zn
Mehlich No. 3	All acid soils	0.2 N CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.013 M HNO_3 + 0.001 M EDTA	P, K, Ca, Mg, Na,B, Cu, Fe, Mn, Zn
AB-DPTA	Alkaline soils	1M NH_4HCO_3 + 0.005 M DTPA at pH 7.6	P, K, Na, Fe, Mn, Zn, As, Cd, NO_3
$CaCl_2$	All soils	0.01 M $CaCl_2$	H (i.e.pH), K, ortho-P, P, Mg, Na, organic C, N, NO_3, NH_4, SO_4-S, S, B, Fe, Cu, Mn, Zn, Cd, Pb, Ni, Al, As, (polyphenols)
Ion-exchange resins /membrames	All soils	Cationic and anionic resin	P, Ca, Mg ,K , S, NO_3, NH_4, Al, Mn, Na, Fe, Zn, Cu

So far, studies on the perspectives of multi-nutrient extractants have focussed mainly on laboratory aspects. Recently, more attention has been given to the interpretation of the amount of nutrient extracted and to the set up of fertilizer recommendations schemes. However, the methods used so far to translate laboratory results of multi-nutrient extractants into fertilizer recommendations do not differ from the 'trial and error' methods used for the development of the classic single soil testing methods. The notion emphasized in this thesis is that the agricultural value of fertilizer

recommendation schemes will increase when nutrient interactions are taken into account. In theory, the use of multi-nutrient extractants may facilitate the study on interactions between nutrients because nutrients are extracted from one and the same soil sample, with one reagent and one extraction procedure. So far this very important aspect has received marginal attention.

An alternative for soil extraction with a chemical reagent, is the use of ion-exchange resins (Table 1). The resins, which have a cationic and/or anionic behaviour, act as a sink for the ions in the solution. After extraction the adsorbed ions are removed from the resin and measured via standard procedures. The perspectives of using resins in (bio)availability studies are promising since adsorption of ions by the resins presents some analogy with nutrient uptake by roots. However, the implementation of the resin method on a laboratory scale seems to be limited: the resin method is time consuming and often considered to be too laborious. Instead of resins it is sometimes possible to use ion-exchange membranes.

10.1.2 $CaCl_2$ procedure

In 1986, Houba and co-workers proposed the use of 0.01 M $CaCl_2$ as a multi-nutrient soil extractant. The perspectives of this procedure are described in Chapter 3. The procedure is applicable to all soils and is simple: air dry soil (< 2mm particle size) is extracted with a solution of 0.01 M $CaCl_2$ (w/v 1:10) at 20°C. After a 2h shaking period, pH is measured in the settling suspension. The solution is centrifuged or filtrated and then various nutrients (fractions) can be measured in the supernatant or filtrate (Houba et al., 2000). There are numerous considerations for choosing $CaCl_2$ as an (multi-nutrient) extraction reagent.

- During extraction the soil suspension has an ionic strength (0.03 M) and pH comparable to that of the soil solution under average field conditions.
- The divalent calcium (Ca) ion causes an effective coagulation in the soil suspension; a high salt concentration, as would be the case with salts of monovalent cations like sodium (Na) and ammonium (NH_4), is unnecessary.

- Since Ca is the primary cation at the adsorption complex of most soils, $CaCl_2$ is a more effective exchanger of other adsorbed cations than solutions with other cations.
- In addition to all important nutrients, various heavy metals and soluble organic carbon, nitrogen, phosphorous and sulphur can be determined as well. Soluble organic compounds may be important for interpreting the influence of extracted metals and for the evaluation of microbiological transformations.
- Since various nutrients and metals are extracted in the same extract, interpretation can easily include mutual interactions.
- The simultaneous measurement of a number of parameters and automation of laboratory labour is attractive from a laboratory-operational point of view. This will reduce the costs for soil testing as well as the rapidity of the $CaCl_2$ program.
- The repeatability and reproducibility of the method are better than that of common (multi- nutrient) soil testing methods.
- The use of chemicals is minimized which is positive from an environmental point of view.
- The electrolyte concentration remains practically constant.
- The measured nutrient concentrations reflect the availability at the pH and ionic strength of the soil since the extractant is an unbuffered solution.
- After an extraction period of 1-2 hours an (adsorption) equilibrium state is attained, which facilitates a soil chemical interpretation of the results.

After the $CaCl_2$ extraction, the concentration of nutrients is determined and this concentration can be used for the set up of a multi-nutrient $CaCl_2$ soil testing program. The necessity of numerous, costly and many years laboratory, pot and field experiments has hindered the development of such $CaCl_2$ program. It has been proposed to convert straightforward the fertilization schemes of conventional procedures into fertilization schemes of the $CaCl_2$ procedure. This conversion should be based on the relationship between the amount of nutrient extracted by the conventional method and the $CaCl_2$ procedure. However, such simple conversion has

several disadvantages. The explained variance of the relationship is often moderate and the coefficients of the regression equation do not or seldom have a plant nutritional or soil chemical meaning. In Chapter 5 a fundamental relationship has been deduced between Mg extracted by conventional Mg extraction procedures and Mg extracted by the $CaCl_2$ procedure. The coefficients in this fundamental relationship have a soil chemical meaning or are related to characteristics of the extraction procedure.

The $CaCl_2$ procedure is well tested and the repeatability and reproducibility of the method are good. Point of discussion is still, as with so many other procedures, the effect of soil drying on the amount of nutrient extracted. In Chapter 4 it is shown that soil drying affects the actual (field) status of pH and many nutrients. Despite this, it is believed that the $CaCl_2$ method can be used as a standardized method to equilibrate the liquid and solid phase of a soil and to define the nutrient composition of the liquid phase.

10.2 Soil chemistry

10.2.1 Soil testing

Soil chemistry studies the (physico-) chemical behaviour of soil constituents. During soil testing, (mixtures of) chemicals are added to a soil sample. The addition of these chemicals affects soil constituents via soil processes like ion exchange, adsorption/desorption, precipitation/dissolution, etc. Therefore, soil testing can be seen as 'applied soil chemistry'.

Since the middle of the twentieth century soil testing has been focussed on the optimization of the relationship between the amount of nutrient extracted and crop response. In contrast to soil chemistry, soil testing was not really focussed on the working mechanisms of nutrient extraction, on a precise characterization of soil nutrient fractions or the modelling of nutrient extraction. This has driven soil chemistry and soil testing apart.

To optimize nutrient management, it must be possible to interpret the amount of soil nutrient extracted via soil testing in terms of the working mechanism of the procedure and soil nutrient fractions that are plant available. Moreover, it should be possible to use the extraction results in soil chemical models and crop growth models. Such use seems only possible when present day soil chemical knowledge and tools are introduced in soil testing.

10.2.2 Soil chemical models

The soil consists of four phases: water (liquid), soil particles (solid), gases and biota. Plant nutrients may be present in each of these phases and in different chemical forms (hereafter called nutrient species). Soil chemistry is mainly focussed on the (physico-) chemical interactions of species in the liquid, solid and gas phases.

Particularly in the middle of the twentieth century many studies have been carried out on the physico-chemical processes that affect the behaviour and occurrence of species in soil, e.g. complexation, hydrolysis, precipitation, dissolution, volatilisation, oxidation, reduction, adsorption and desorption. The effect of these processes on changes in speciation can be described mathematically under equilibrium conditions (Bolt, 1982; Sposito, 1994). With these mathematical descriptions it is possible to calculate the effect of e.g. addition or withdrawal of species on speciation and its distribution. In the second half of the twentieth century the mathematical descriptions have been incorporated into computer models. These models have simplified the execution of time-consuming calculations. With present day computer technology it is possible to calculate almost instantaneously speciation in multi-element soil-water-gas systems under varying conditions. Well-known soil chemical models are MINEQL, GEOCHEM and ECOSAT (Keizer and Van Riemsdijk, 1998). With some of these models it is possible to calculate speciation under non-equilibrium conditions.

Figure 1 gives a simple presentation of the set up of a soil chemical model. The model consists of an input module, a calculation module and an output module. In the input module the user characterizes the soil system under study and defines his problem or question. Subsequently, this information is used in the calculation module to perform

the necessary system specific calculations. Finally, the results of the calculations are presented via the output module.

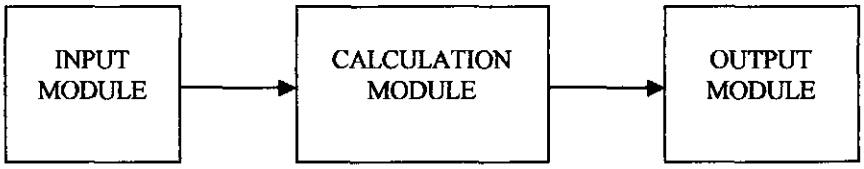


FIGURE 1. Simplified presentation of the set up of a soil chemical model.

The system characteristics that should be filled in in the input module depend on the type of problem or question, and on the type of calculations that are necessary to produce the desired results. In general, characterization of a soil-water system consists of a characterization of the liquid phase, the solid phase, the total system and the choice of the calculation rules describing the prevailing processes. Characteristics of the liquid phase are e.g. pH, ionic strength, total element concentration and DOC (dissolved organic carbon).

Theoretically, soil chemical models can be used to calculate nutrient speciation and distribution over the liquid and adsorptive phase during soil testing. However, the usefulness of soil chemical models for this is limited thus far because the necessary characterization of the liquid and solid phase of soils during soil testing has been unknown so far.

The 0.01 M $CaCl_2$ soil extraction procedure is executed under well-defined and controlled conditions. In Chapter 2 it is shown that it is likely that an (adsorption) equilibrium state is reached during the $CaCl_2$ procedure when extraction time is more than one hour. This (adsorption) equilibrium state makes that soil chemical models can be used to characterize the liquid and solid phase during $CaCl_2$ extraction. With modern analytical techniques it is possible to characterize the composition of the liquid phase after filtration. The studies presented in this thesis have shown that it is also possible to characterize the solid phase during $CaCl_2$ extraction. In Chapter 6 it is described how the actual CEC of the solid phase during the 0.01 M $CaCl_2$ procedure

can be estimated using pH and content of organic carbon and clay. In Chapter 8 the selectivity coefficients are deduced of Ca, Mg and K exchange reactions during $CaCl_2$ extraction. In the same Chapter a procedure is proposed to calculate the amounts of soil exchangeable Ca, Mg and K during the $CaCl_2$ procedure. In Chapter 7 it is shown that exchangeable K is a good indicator of the lower boundary of the pool of plant available K. In the studies the amount of exchangeable cations is determined according the unbuffered 0.01 M $BaCl_2$ method. This $BaCl_2$ method is discussed in Chapter 9. Based on the results obtained in the studies, it is stated that the 0.01 M $CaCl_2$ procedure may promote the use of soil chemical models for characterization of plant available soil nutrients and for optimization of nutrient management.

10.2.3 Combined use soil chemical model and $CaCl_2$ procedure

This section presents examples showing the perspectives of a combined use of a soil chemical model and the $CaCl_2$ procedure. It is illustrated how a soil chemical model can be used to characterize the solid and liquid phases of the soil and how it can be used to examine the sensitivity of various factors that may determine the results of the $CaCl_2$ procedure.

The examples deal with nutrient distribution over the liquid and adsorptive phase and focus on the cationic nutrients Ca^{2+}, Mg^{2+} and K^{+}. These cations are dominant in non-acid agricultural soils in The Netherlands. It is assumed that the cations show an interaction with negatively charged adsorption sites located at the adsorptive phase.

The studies have been carried out with two soil types: soil A and soil B. The charge of the adsorption sites in both soils is 0.1 mol(-) kg^{-1} dry soil. The composition of the soil solution is the same for both soils and the cations adsorbed at adsorptive phase are in equilibrium with this soil solution. Soil B has two types of adsorption sites: B-I and B-II. B-II shows a higher affinity for K compared to B-I. Adsorption sites of soil A are equal to that of B-I and show the same affinity for the cations under study. The total charge of B-I and B-II is 0.075 and 0.025 mol(-) kg^{-1} dry soil, respectively. In the model calculations it is assumed that the soils have no adsorption sites for negatively charged ions. Most soil characteristics used for soil A and B are measured values from an 'average' agricultural soil. The exchange processes in the model calculations obey

the Gaines & Thomas approach for ion exchange. Details on the model input characteristics and model calculations are omitted. The emphasis here is conceptual rather than focussing on the absolute value of the results of the model calculations.

Example 1: Calculation nutrient speciation soil liquid phase

In most current soil testing programs the total nutrient concentration in the liquid phase is determined without reference to its chemical speciation. Determination of speciation is sometimes possible but time-consuming and expensive. With help of a soil chemical model the speciation of the liquid phase can be calculated.

TABLE 2. Speciation of the liquid phase of soil A. In the liquid phase the dominant anions are Cl, NO_3 and ortho-P. Concentrations are presented as log(mol l^{-1}).

Species	Concentration	Species	Concentration
H^+	-6.28	Mg^{2+}	-3.61
OH^-	-7.68	$MgHPO_4$	-7.10
Ca (total)	-3.46	$MgH_2PO_4^+$	-7.53
Ca^{2+}	-3.46	$MgOH^+$	-8.88
$CaHPO_4$	-7.01	$MgPO_4^-$	-9.41
$CaH_2PO_4^+$	-7.42	N (total)	-3.89
$CaPO_4^-$	-9.32	NO_3^-	-3.89
$CaOH^+$	-9.99	Na (total)	-4.41
Cl (total)	-2.96	Na^+	-4.41
K (total)	-4.18	P (total)	-5.21
K^+	-4.12	$H_2PO_4^-$	-5.29
Mg(total)	-3.68	HPO_4^{2-}	-6.13

Table 2 gives the calculated speciation in the liquid phase of soil A. Numerous species can be distinguished in the liquid phase but concentrations are most times low. The ions Ca^{2+}, Mg^{2+}, K^+ and Na^+ are the cationic species with the highest concentrations. Although the effect of speciation on plant nutrient availability is not clear yet, this example shows that the soil chemical model is a practical tool to estimate speciation in the liquid phase.

Example 2: The effect of high affinity sites on cationic composition adsorptive phase

According to the Gaines & Thomas approach for ion exchange, a relationship exists at (adsorption) equilibrium between the concentration of cationic species in the liquid phase and the equivalent fractions of these species at the adsorptive phase. Under equilibrium conditions it is possible to calculate the cationic composition of the adsorptive phase with a soil chemical model, when the cationic composition of the liquid phase, the selectivity coefficients of the relevant cation exchange reactions and the total negative charge of the adsorptive phase are known.

In this example the cationic composition of the adsorptive phases of soil A and B has been estimated based on the cation concentrations of the liquid phase of the soils.

TABLE 3. Adsorption of Ca, Mg, K and Na at the adsorptive phase of soil A (A-I) and at the different adsorptive phases of soil B (B-I and B-II). Adsorption is calculated from the cation concentration in the liquid phase using standard selectivity coefficients. Results presented as log(mol kg^{-1} soil).

Element	Soil A		Soil B		
	A-I	Total	B-I	B-II	Total
Ca	-1.44	-1.44	-1.57	-2.07	-1.45
Mg	-1.87	-1.87	-1.99	-2.49	-1.87
K	-3.21	-3.21	-3.34	-2.83	-2.72
Na	-4.14	-4.14	-4.27	-4.76	-4.15

B-I represents 75 percent of the total negative charge of soil B. Therefore the amounts of Ca, Mg and Na at B-I are larger than that at B-II (Table 3). Although the total negative charge of B-II is much smaller than of B-I, K adsorption at B-II is much higher than at B-I. This can be explained by the high affinity for K of B-II compared to B-I. Because of the increased K adsorption in the adsorptive phase of soil B the total amount of adsorbed Ca, Mg and Na in soil B is correspondingly lower than in soil A. This example shows that when the cation concentrations in the liquid phase are the same, cation adsorption at the adsorptive phase may differ because of differences in the affinity of particular adsorption sites for one of the cations present. The soil chemical model can be used to quantify the effect of high affinity sites on distribution.

Example 3: Effect $CaCl_2$ soil extraction on cationic composition adsorptive phase

In the $CaCl_2$ soil extraction procedure a 0.01 M $CaCl_2$ solution is added to a dry soil (w/v=1:10) and then shaked during 2 h. The addition of Ca results in the replacement of (part) of the cations originally present at the adsorptive phase. With a soil chemical model it is possible to estimate the effect of Ca addition via $CaCl_2$ on the composition of the liquid and adsorptive phase after extraction. In this example such calculations have been carried out for soil A.

TABLE 4. Adsorption of Ca, Mg, K and Na at soil A before and after soil extraction according to the $CaCl_2$ procedure. Cation adsorption is presented in $mol.kg^{-1}$ soil and as % charge occupation (= 100*total charge of the adsorbed cation/total negative charge of A-I).

Element	Before extraction		After extraction	
	Amount	Occupation	Amount	Occupation
Ca	$3.60 * 10^{-2}$	72.0	$4.66 *10^{-2}$	93.1
Mg	$1.37 * 10^{-2}$	27.3	$3.37 *10^{-3}$	6.8
K	$6.03 * 10^{-4}$	0.6	$1.02 *10^{-4}$	0.1
Na	$7.08 * 10^{-5}$	0.1	$2.76 *10^{-6}$	0.0

The addition of Ca leads to an increase of the Ca adsorption at the adsorptive phase from $3.60*10^{-2}$ $mol.kg^{-1}$ before extraction to $4.66*10^{-2}$ $mol.kg^{-1}$ after extraction. After extraction Ca occupies more than 93% of the negative charge of A-I. This adsorption of Ca resulted in the replacement of 75, 83 and more than 95 % of the Mg, K and Na originally present at A-I, respectively. Ca and Mg are the dominant ions at the adsorptive phase. The results show that Ca replaces K and Na more easily than the divalent cation Mg. The cations replaced from the adsorptive phase are dissolved in the liquid phase (data not presented).

The nutrient concentration of the liquid phase can be used as a nutrient availability index. Table 4 shows that the $CaCl_2$ procedure does not extract all cations originally present at the adsorptive phase. This means that the concentration of extracted cations underestimates the amount of plant available cation (assuming that the cations retained

at the adsorptive phase remain exchangeable and thus potentially plant available). The model may provide estimates for these amounts.

Example 4: Effect of shaking ratio on the distribution of cations

In this example the effect is studied of shaking ratio in the $CaCl_2$ procedure on the distribution of Ca, Mg, K, Na and Cl over the liquid and adsorptive phases. Soil A is subjected to shaking ratios of 1:0.3, 1:3, 1:10 and 1:30 (w/v).

When shaking ratio increases extra Ca and Cl is added to the soil. As a result the sum of Ca in the adsorptive and liquid phase increases when shaking ratio increases (Figure 2a). Cl shows no interaction with the adsorptive phase and therefore Cl will remain in the liquid phase. Ca shows an interaction with the adsorptive phase and therefore part of Ca added will adsorb at the adsorptive phase. At a shaking ratio of 1:30 Ca occupies more than 95 percent of A-I, the adsorptive phase. However, the majority of Ca remains in the liquid phase.

The total amounts of Mg and K in the liquid and adsorptive phase remain constant irrespective of the shaking ratio (Figure 2b and 2c). At a low shaking ratio considerable amounts of Mg and K are retained at the adsorptive phase but when the shaking ratio increases, this amount decreases sharply. At the same time, the amounts of Mg and K in the liquid phase increase sharply. For Na the results are comparable to Mg and K.

The $CaCl_2$ procedure recommends a shaking ratio of 1:10 (w/v). Figure 2 shows that at this shaking ratio the amounts of Mg and K retained at the adsorptive phase are much higher than at a shaking ratio of 1:30. This means that $CaCl_2$ does not replace all Mg and K (and Na) when shaking ratio is low. A shaking ratio of 1:0.3 is comparable to the soil:water ratio under field conditions. Figure 2 shows that under such conditions only part of the total amounts of Mg and K in the soil is in the liquid phase. This example clearly shows that when a soil system is characterized with the standard $CaCl_2$ procedure, then the soil chemical model can be used to calculate the effect of shaking ratio on cation distribution under e.g. under field conditions.

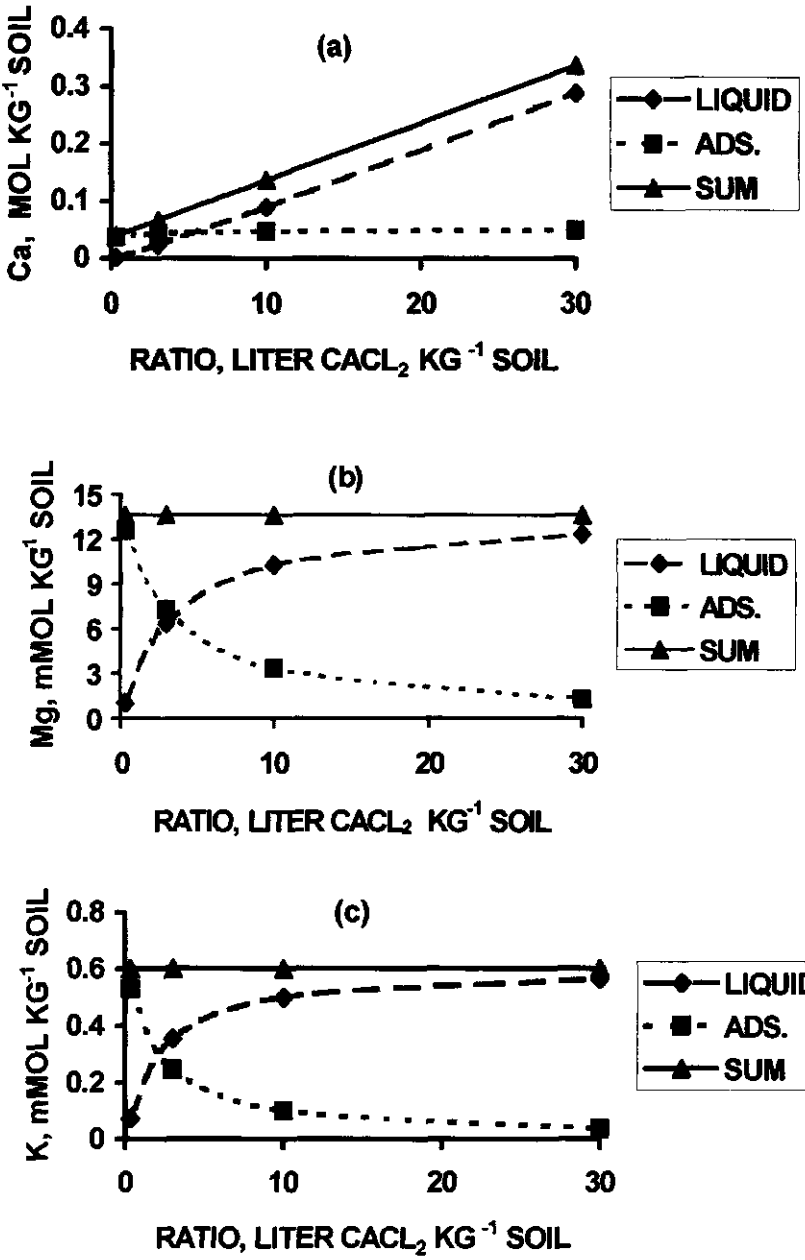


FIGURE 2. The effect of shaking ratio on the amounts of Ca (a), Mg (b) and K (c) in the liquid and the adsorptive phases of soil.

Example 5: Effect of $CaCl_2$ concentration on cation distribution

In this example, the effect of $CaCl_2$ concentration in the $CaCl_2$ procedure on the distribution of Ca, Mg, K, Na and Cl is studied. Table 5 gives the calculated distribution of Ca, Mg, K, Na and Cl over the liquid and adsorptive phase when soil A is extracted according to the $CaCl_2$ procedure with solutions of 0.005, 0.01 and 0.03 M $CaCl_2$. It was assumed that differences in ionic strength have no effect on system characteristics.

Table 5 clearly shows that the $CaCl_2$ concentration in the extractant has a considerable effect on nutrient distribution. The Mg, K and Na concentration in the liquid phase increases when $CaCl_2$ concentration increases. Furthermore, the model calculations show that the amounts of Mg, K and Na retained at the adsorptive phase decreases when $CaCl_2$ concentration increases. Cl shows no interaction with the adsorptive phase and therefore all Cl added via $CaCl_2$ remains in the liquid phase.

TABLE 5. The effect of the use of 0.005 M, 0.01 M and 0.03 M $CaCl_2$ solutions in the $CaCl_2$ procedure on the distribution of Ca, Mg, K, Na and Cl over the liquid and adsorptive phase of soil A. Concentrations of the liquid phase in log(mol.10 l^{-1}) and at the adsorptive phase in log(mol kg^{-1} dry soil).

		$CaCl_2$ concentration		
Element	Phase	0.005	0.01	0.03
Ca	Liquid	-1.38	-1.05	-0.54
	Adsorptive	-1.35	-1.33	-1.31
Mg	Liquid	-2.09	-1.98	-1.91
	Adsorptive	-2.26	-2.47	-2.88
K	Liquid	-3.33	-3.30	-3.27
	Adsorptive	-3.87	-3.70	-4.20
Na	Liquid	-4.17	-4.17	-4.16
	Adsorptive	-5.42	-5.56	-5.80
Cl	Liquid	-1	-0.70	-0.22

The total concentration of NO_3 and ortho-P in the liquid phase was independent of the $CaCl_2$ concentration used: these anions show no interaction with the adsorptive phase.

This example clearly shows that the soil chemical model can be used to estimate the effect of $CaCl_2$ concentration on the distribution of cations over the liquid and adsorptive phases of the soil system.

Example 6: The effect of the size of the CEC on cation distribution

In this example, the effect has been investigated of varying CEC values of the adsorptive phase of soil A on cation distribution. The CEC of the 'test soils' was 0.02, 0.05 and 0.12 mol(-) kg^{-1} dry soil. The equivalent fraction (total positive charge cation / total negative charge adsorptive phase) of Ca, Mg, K and Na at the adsorptive phase and the concentration of the cations in the liquid phase were the same for all 'test soils' under field conditions.

TABLE 6. The effect of CEC values of soil A of 0.02, 0.05 and 0.12 mol(-) kg^{-1} on the equivalent fraction of Ca, Mg, K and Na remaining at the adsorptive phase after 0.01 M $CaCl_2$ extraction. Equivalent fraction = total positive charge cation / total negative charge adsorptive phase.

	CEC, in mol(-) kg^{-1} dry soil		
Element	0.02	0.05	0.12
Ca	0.983	0.961	0.921
Mg	0.016	0.038	0.078
K	0.0000	0.0005	0.0012
Na	0.0000	0.0000	0.0000

Table 6 gives the equivalent fraction of Ca, Mg, K and Na at the adsorptive phase after extraction according to the $CaCl_2$ procedure. The replacement of Na and K is almost complete irrespective of the size of the CEC. The replacement of the divalent cation Mg is not complete and related to the size of the CEC: the Mg equivalent fraction after extraction is 0.016 and 0.078 at CEC values of 0.02 and 0.12 mol(-) kg^{-1} soil, respectively. This example clearly shows that the soil chemical model can be used to

estimate the effect of the size of the CEC on the equivalent fraction of Ca, Mg, K and Na at the adsorptive phases.

Example 7: Effect high affinity sites on cation distribution during $CaCl_2$ extraction

In example 2, the effect of high affinity sites in soil B on the distribution of Ca, Mg and K was estimated and compared to soil A which had no such high affinity sites. In this example, soil A and B were extracted according to the $CaCl_2$ procedure and the effect of the presence of different high affinity sites on the distribution of cations after extraction is determined. The total amount of K is more than three times larger in soil B than in soil A (Table 7). The higher amount in soil B can be explained by the large amount of K at the high affinity site B-II.

TABLE 7. Total amount of Ca, Mg, K and Na in soils A and B before extraction, and the distribution of Ca, Mg, K and Na over the liquid phase and the adsorptive phase in soil A (A-I) and soil B (B-I and B-II) after extraction. B-II shows a high affinity for K. Results in liquid phase in log (mol. 10 l^{-1}), at A-I in log(mol kg^{-1} soil), at B-I in log(mol 0.75 kg^{-1} soil), and at B-II in log(mol 0.25 kg^{-1} soil).

Element	Before extraction		After extraction				
	Soil A	Soil B	Soil A		Soil B		
			Liquid	A-I	Liquid	B-I	B-II
Ca	-1.44	-1.44	-1.05	-1.33	-1.05	-1.46	-1.94
Mg	-1.87	-1.87	-1.99	-2.47	-1.99	-2.60	-3.09
K	-3.21	-2.72	-3.30	-3.99	-2.94	-3.75	-3.23
Na	-4.15	-4.15	-4.17	-5.56	-4.17	-5.69	-6.17

Because Ca is added to the soils via $CaCl_2$ the total amount of Ca after extraction exceeds the total amount of Ca before extraction. After extraction, the Ca equivalent fraction at A-I, B-I and B-II is 0.93, 0.93 and 0.91, respectively. In soil A about 17 percent of the total amount of K is retained at the adsorptive phase and in soil B about 40 percent. The K equivalent fraction at B-I is low and comparable to the K equivalent fraction at A-I. However, the K equivalent fraction at B-II is about 10 times higher than at B-I. This much higher fraction results from the high affinity of B-II for K.

After extraction, 83 percent of the total amount of K in soil A and 60 percent of total K in soil B is present in the liquid phase.

In this example it was assumed that K affinity of B-II was two times higher than K affinity of A-I and B-I. Although the increase in K affinity is relatively small, there is a clear effect on K-distribution. Some clay minerals contain adsorption sites with a very high affinity for K ions. In soils containing these minerals, the availability of K bound to these sites is extremely low (K-fixing soils). When this type of soil is extracted according to the $CaCl_2$ procedure, Ca will not replace all K adsorbed at the high affinity sites and as a result K content in the liquid phase will be (very) low.

Example 8: Effect size CEC on interpretation $CaCl_2$ extraction results

Foregoing examples have shown that $CaCl_2$ does not replace all cations originally present at the adsorptive phase. This is of importance for the interpretation of the concentration of nutrient extracted. In this example, the cation concentration remaining at the adsorptive phase is estimated for three soils with different CEC values but with the same cationic composition of the liquid phase after extraction as soil A. The CEC of the adsorptive phases was 0.05, 0.1 and 0.15 mol(-) kg^{-1} dry soil, respectively. All adsorption sites have the same affinity for the cations.

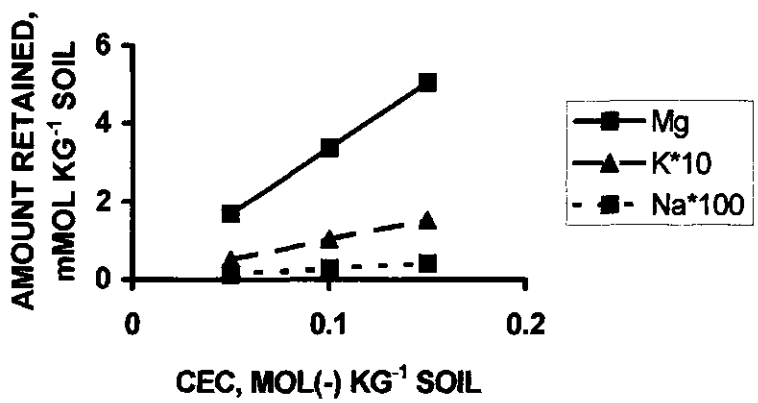


FIGURE 3. Relationship between the CEC and the amount of Mg, K and Na retained at the adsorptive phase after $CaCl_2$ extraction.

Figure 3 gives the relationship between the CEC and the calculated Mg, K, and Na concentrations at the adsorptive phase after $CaCl_2$ extraction. The model calculations show that the concentrations of Mg, K and Na remaining at the adsorptive phase increases when CEC increases. In this study the calculated increase is 50% when CEC increases with 0.05 mol(-) kg^{-1} soil.

The calculations show that the cation concentration of the liquid phase after $CaCl_2$ extraction is no indicator of the amount of cation retained at the adsorptive phase. As the CEC of the adsorptive phase increases the concentration of cations remaining at the adsorptive phase increases. This example shows that the soil chemical model leads to a better interpretation of $CaCl_2$ soil extraction results.

Example 9: Effect Mg concentration on cation equivalent fraction adsorptive phase

In this example, the effect of Mg concentration in the liquid phase of soil A after $CaCl_2$ extraction on the cation concentration of the adsorptive phase is investigated. In the model calculations it is assumed that the composition of the liquid phase is the same, except for Mg (and Cl which acts as the counterion for Mg) and that there was no effect of ionic strength on exchange behaviour.

The model calculations show that a higher Mg concentration in the liquid phase leads to an increase of the Mg equivalent fraction and a decrease of the Ca equivalent fraction at the adsorptive phase (Table 8). A higher Mg concentration of the liquid phase resulted also in lower K and Na equivalent fractions at the adsorptive phase.

TABLE 8. The effect of Mg concentration (in mol l^{-1}) in the liquid phase of soil A on the equivalent fractions of Ca, Mg, K and Na at the adsorptive phase after extraction. The total concentration of cations, i.e. cations in liquid phase plus adsorptive phase, was the same except for Mg. Equivalent fraction = total positive charge cation / total negative charge adsorptive phase.

	Equivalent fraction			
Mg conc.	Ca	Mg	K	Na
$3.386*10^{-3}$	0.976	0.023	0.001	0.000
$1.026*10^{-2}$	0.931	0.067	0.001	0.000
$3.078*10^{-2}$	0.820	0.178	0.001	0.000

The model calculations show that changes in the concentration of one cation in the liquid phase affect the cation equivalent fractions at the adsorptive phase. This may affect the interpretation of $CaCl_2$ extraction results.

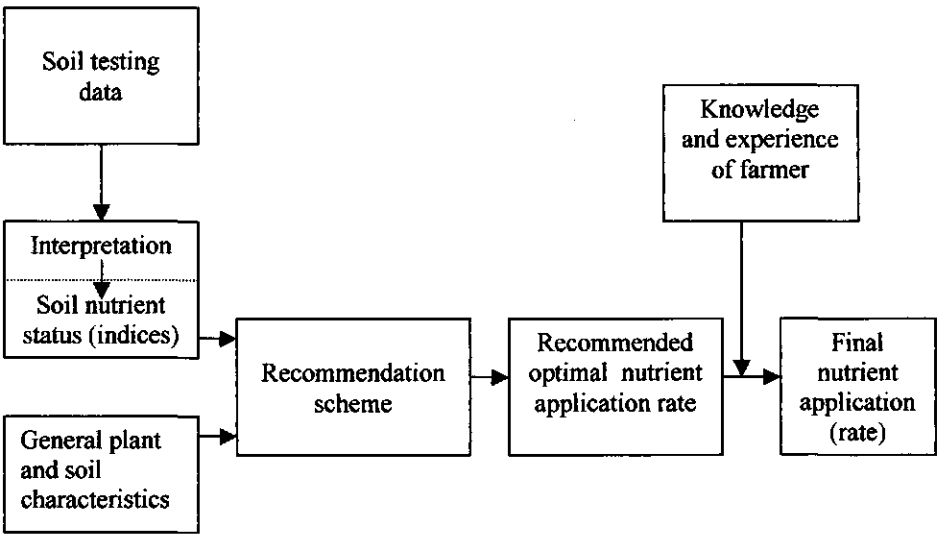
Practical value of the examples
The examples were restricted to two test soils with one (or two) type(s) of negatively charged adsorption sites. However, most agricultural soils contain positively charged adsorption sites in the adsorptive phase as well. These sites adsorb anions. It is possible to carry out the same type of calculations with the soil chemical model for anions as described for cations. In this way it is possible to estimate e.g. the effect of the Cl addition via the $CaCl_2$ reagent on the exchange of negatively charged ions at the adsorptive phase.
In the examples the model calculations were focussed on nutrients like Ca, Mg, K, Na and Cl. The same type of model calculations can be used to calculate speciation and distribution of other (nutrient) elements, e.g. Cu, Zn, Fe, Al, Mn. When a soil containing these elements is characterized e.g. via the $CaCl_2$ procedure, then the soil chemical model can estimate the effect of e.g. adsorption sites at Fe- and Al-(hydr)oxides on P availability or the effect of Zn adsorption at dissolved organic matter (DOC) on Zn availability. For these calculations a mathematical description of the adsorption process at this type of sites is necessary.
In the examples it was assumed that an equilibrium state exists. However, the model can also be used to estimate the effect of (kinetically determined) soil processes where every time step nutrients are released or fixed. In that situation, calculations should be repeated for each time step.

10.3 Decision-making in nutrient management

10.3.1 Framework nutrient management

Nutrient management is the prime factor determining nutrient efficiency, nutrient losses and food quality. Nutrient management on agricultural farms has to comply with an increasing number of demands and border conditions of society and industry (FAO, 1999; European Community, 2000; FAO, 2001).

FIGURE 4. General presentation of nutrient management decision-making in current farm management.



Nutrient management can be defined as "specialized activities dealing with all nutrient sources and transformations within a defined system so as to achieve both economic and environmental targets" (Oenema and Pietrzak, 2002). Figure 4 gives a general scheme of nutrient management decision-making in current farm management. After chemical analysis, soil testing data are interpreted resulting in a characterization of the soil nutrient status. Subsequently, a recommendation scheme is used to determine the optimal nutrient application rate. In such scheme the soil nutrient status and plant and soil characteristics are input variables.

The recommended nutrient application rate in combination with the knowledge and experience of the farmer determines the final nutrient application rate. Disadvantage of this nutrient management decision-making is that:

- soil testing is carried out annually or once a crop rotation. A dynamic and continuous decision-making is therefore not possible;

- the basis for the interpretation of soil testing data and the recommendation schemes is the statistical analysis of numerous field and pot experiments ('trial and error' method);
- the fundamentals of soil-plant-nutrient relationships, which determine the actual nutrient requirements are minimally incorporated;
- the procedure does not profit from present day scientific knowledge about soil-plant-nutrient relationships, computer technologies for data collection and data processing, new analytical techniques and optimization procedures.

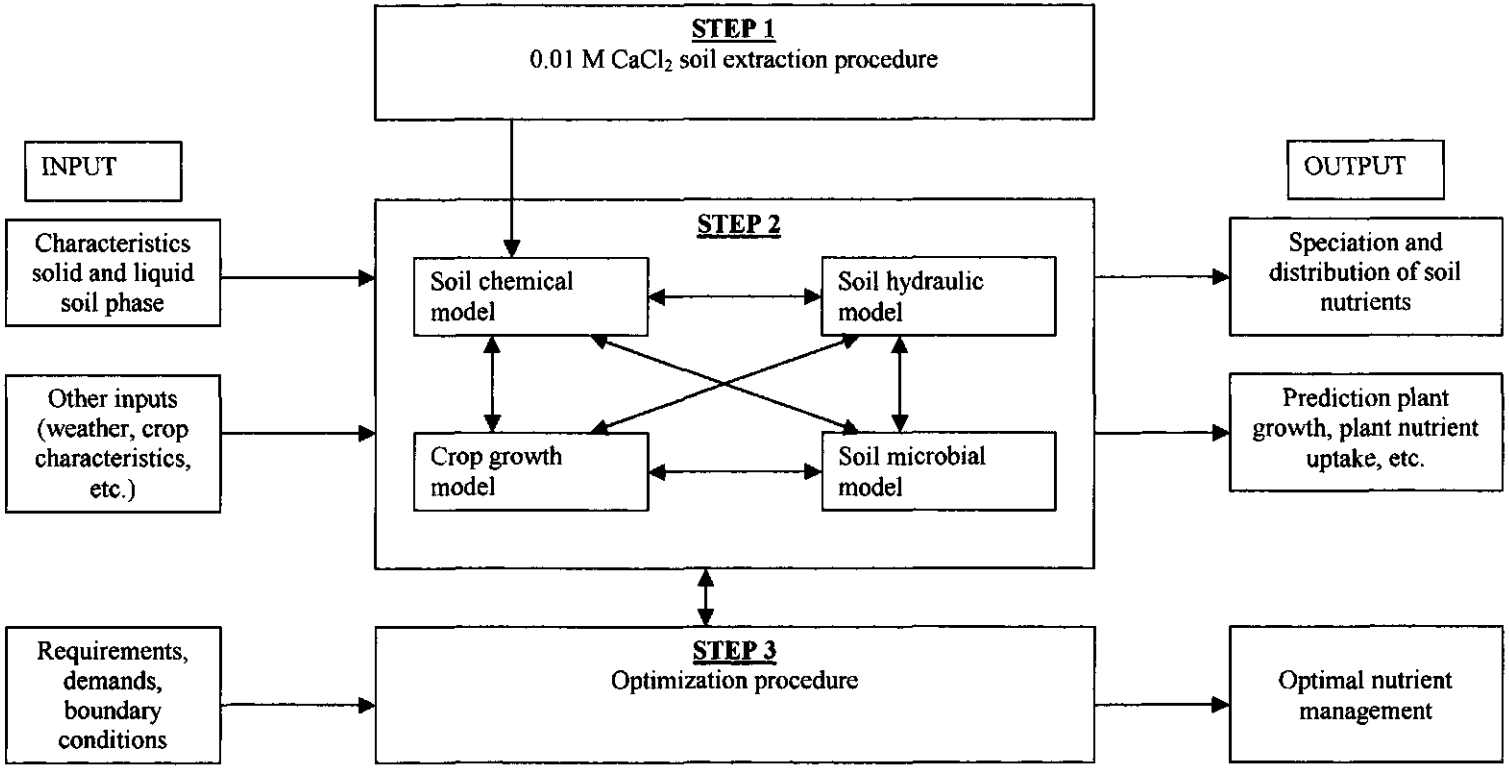
Figure 5 provides a framework for adjusted nutrient management decision-making. Three steps can be distinguished.

In step 1 the 0.01 M $CaCl_2$ procedure is used as a standard method to extract nutrients from a soil sample. After a 2 h shaking period, when an (adsorption) equilibrium is attained, pH and nutrient concentration are determined in the liquid phase according to standard procedures. The pH and nutrient concentrations determined are then used as input in a soil chemical model.

In step 2 the effect of (proposed or expected changes in) the actual (nutrient) status of the soil-plant system on crop growth, nutrient status, soil nutrient fractions, etc. is calculated. For these calculations a soil chemical model, a crop growth model, a microbiological model and a soil hydraulic model are coupled. Each model contain a mathematical description of related relevant processes in the soil-plant system.

The microbial model in step 2 is relevant when e.g. N, P and S availability is studied. Namely, organic N, P or S added to soils via crop residues, catch crops or organic fertilizers becomes available for plant uptake when it is converted into mineral forms by microbes. The soil chemical model calculates soil nutrient fractions and speciation, e.g. after plant nutrient uptake or addition of nutrients via mineral or organic fertilizers. The soil hydraulic model becomes relevant when e.g. transport processes of water, nutrients and air are studied, e.g. after rain showers.

FIGURE 5. Framework of mechanistic relationships in nutrient management decision-making. Inputs and outputs of the soil microbial and soil physical models are not detailed.



The crop growth model may calculate e.g. biomass production, nutrient uptake in course of time, (total) nutrient use efficiency, changes in the pool of plant available nutrients, etc. The pool of plant available nutrient is an important growth-determining factor in this model. The nutrient speciation and distribution as calculated with the soil chemical model can be used to define this pool.

Step 3 encompasses the determination of e.g. optimal nutrient application rate. In this step a mathematical procedure optimizes nutrient management and nutrient application using data on farm profitability, crop growth, soil nutrient status, crop production and crop quality and legislative and environmental boundary conditions. To carry out the necessary calculations in step 2, the models need relevant input information, e.g. weather conditions, soil and crop characteristics, $CaCl_2$ extraction data, etc. Moreover, the calculation results of one model can be used as input in one of the other models.

The proposed concept of nutrient management includes several inter-connected and innovative aspects:

- the use of the $CaCl_2$ soil extraction procedure to standardize the equilibration of the liquid and solid phase of the soil under study (step 1);
- the use of $CaCl_2$ soil extraction data in a soil chemical model and the calculation of nutrient speciation and distribution (step 2);
- a mechanistic approach of the soil-plant-nutrient relationships in agricultural soil using a soil chemical, soil microbial, soil hydraulic and crop growth model (step 2);
- the use of a mathematical procedure to optimize nutrient management taking into account farm specific and agricultural demands and legislative and environmental boundary conditions (step 3).

The building blocks of the framework, i.e. the 0.01 M $CaCl_2$ extraction procedure, a soil chemical model, a crop growth model, a microbial model, a soil hydraulic model and optimization procedures, are available but still need to be integrated into a computer model. Further, the framework has to be tested using data from laboratory, pot and field experiments.

10.3.2 Examples showing perspectives framework

This section presents some examples showing the perspectives of the proposed framework. The examples are restricted to the use of the $CaCl_2$ procedure and the soil chemical model in combination with a crop growth model or a soil hydraulic model. See section 10.2.3. for a description of soil A and B and their $CaCl_2$ extraction results.

Example 1: Effect of fertilization on cation distribution

This example studies the effect of fertilization with 300 kg ha^{-1} K on the distribution of Ca, Mg, K, Na and Cl over the liquid phase and adsorptive phase of soil A. K is added via KCl and the applied K is homogeneously distributed over the top 5 cm of the plough layer. Table 9 gives the results of the model calculations.

Addition of 300 kg ha^{-1} K via KCl leads to a small decrease of the Ca, Mg and Na concentrations at the adsorptive phase but to a considerable increase of the K concentration. The addition of 300 kg ha^{-1} K resulted into a higher content of all nutrients in the liquid phase. As expected, the increase in the liquid phase was considerable for K and Cl. This example shows that the effect of the addition of fertilizers on the distribution of cations can be calculated using the soil chemical model in combination with 0.01 M $CaCl_2$ procedure.

TABLE 9. Effect of fertilization with 0 and 300 kg ha^{-1} K on the distribution of Ca, Mg, K, Na and Cl over the liquid and adsorptive phase of soil A. Soil water content is set at 0.3 kg water kg^{-1} soil. Results of the adsorptive phase are expressed in log (mol kg^{-1} soil) and the results of the liquid phase in log(mol 0.3 l^{-1} water).

		K-application, kg ha^{-1}	
Phase	Element	0	300
Adsorptive	Ca	-1.443	-1.448
	Mg	-1.863	-1.872
	K	-3.219	-2.735
	Na	-4.149	-4.216
Liquid	Ca	-3.979	-3.310
	Mg	-4.201	-3.535
	K	-4.699	-3.879
	Na	-4.932	-4.659
	Cl	-3.485	-2.774

Example 2: Effect of plant nutrient uptake on nutrient distribution

In this example the effect of K uptake on the K concentration of the liquid phase and adsorptive phase has been calculated for soils A and B. Total K content in soil B is higher than in soil A. In both soils the water content is set at 0.3 kg water kg^{-1} dry soil. Figure 6a gives the K uptake during a growing period of 100 days as calculated with the crop growth model. In 100 days 200 kg K ha^{-1} is taken up.

At the start, the K concentration in the liquid phase is higher in soil B than in soil A, because the K status of soil B is higher (Figure 6b). In the first 20-30 days of the growing period when K uptake is small, K concentration in the liquid phase lowers gradually. In the period from day 30 to 75, K uptake is high and K concentration in the liquid phase lowers quickly. In the period from day 75 to 100, K uptake levels off and as a result K concentration of the liquid phase levels off. The decrease in K concentration in soil B is higher than in soil A and a direct result from the high affinity sites B-II. These sites will only release enough K when K concentration in the liquid phase is much lower compared to A-I and B-I. Figure 6c shows the time course of the K concentration at the adsorption sites A-I in soil A and at the adsorption sites B-I and B-II in soil B. K concentration at B-II is much higher than at B-I although the total negative charge of B-II is only 0.025 mol(-) kg^{-1} soil. In soil B the major part of K is released from B-II. The decrease in K concentration of B-I is relatively small.

This example shows that the combined use of the $CaCl_2$ extraction procedure, a soil chemical model and a crop growth is promising for estimating nutrient concentration of the liquid phase and adsorptive phase CEC during a growing season.

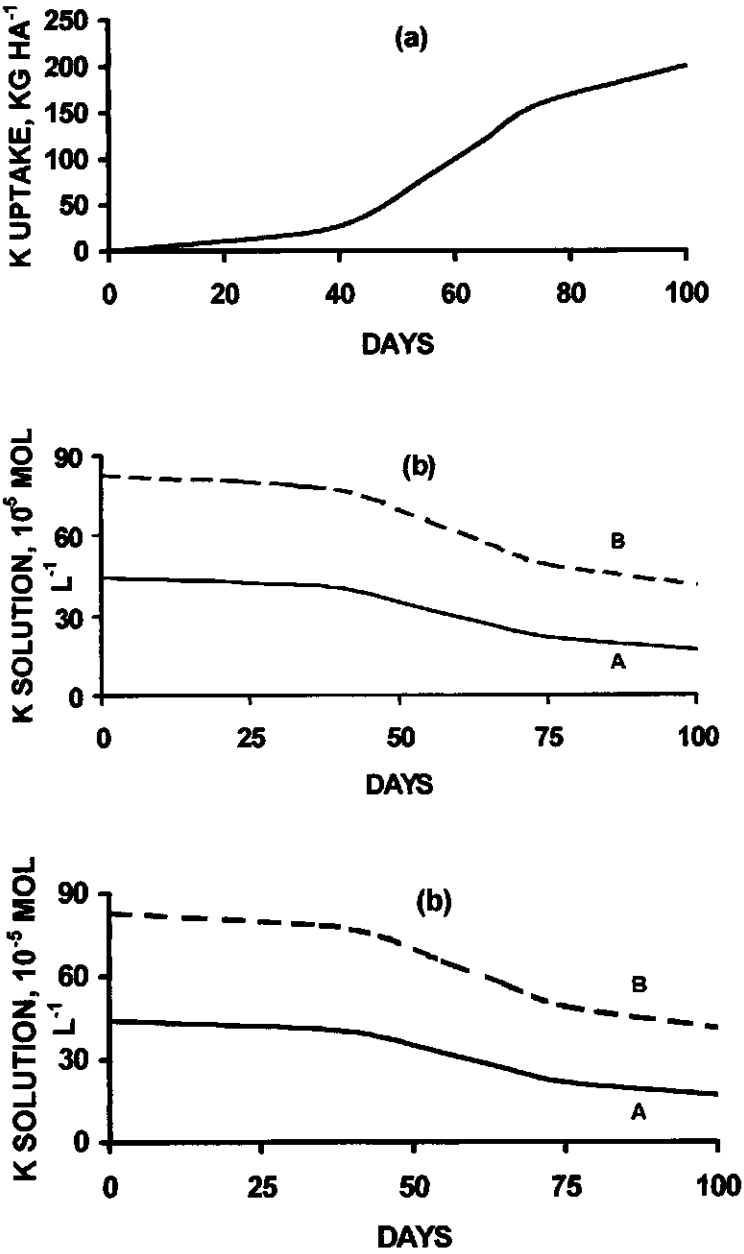


FIGURE 6. The K uptake of a crop during a growing period of 100 days (a), the K concentration of the soil solution in soil A and B (b), and the calculated K concentration at A-I, B-I and B-II (c).

Example 3: Effect soil moisture content on nutrient distribution, speciation and leaching

In this example the effect of varying moisture content, i.e. 1, 0.5 and 0.1 kg kg^{-1} dry soil, on speciation, distribution and leaching losses is estimated for the top 5 cm of the plough layer of soil A. Water holding capacity of soil A is 0.5 kg kg^{-1} dry soil.

Lowering moisture content resulted in a (small) decrease of the Ca and Mg concentration at the adsorptive phase and a small increase of K and Na concentration (Table 10). In the liquid phase the concentration of all species increased when moisture content lowered. Lowering moisture content to 0.5 and 0.1 kg water per kg soil, resulted in the formation of $CaHPO_4$, $CaH_2PO_4^+$, $MgHPO_4$ and $MgH_2PO_4^+$. The effects of these changes in speciation on plant nutrient availability need more research.

TABLE 10. Effect of moisture content on the cation concentration in the adsorptive phase in mol kg^{-1}, and on the presence and concentration of species in the liquid phase in log(mol l^{-1} water). Species in the liquid phase are omitted when log(mol l^{-1} water) was lower than -7.

		Moisture content, kg. kg^{-1} dry soil		
Phase	Species	1	0.5	0.1
Adsorptive	Ca	$3.602*10^{-2}$	$3.601*10^{-2}$	$3.600*10^{-2}$
	Mg	$1.365*10^{-2}$	$1.364*10^{-2}$	$1.363*10^{-2}$
	K	$6.026*10^{-4}$	$6.202*10^{-4}$	$6.459*10^{-4}$
	Na	$7.079*10^{-5}$	$7.878*10^{-5}$	$9.317*10^{-5}$
Liquid	H^+	-6.281	-6.118	-5.705
	Ca^{2+}	-3.457	-3.146	-2.433
	$CaHPO_4$		-6.590	-5.545
	$CaH_2PO_4^+$		-6.830	-5.727
	Cl^-	-2.963	-2.662	-1.963
	K^+	-4.177	-4.009	-3.635
	Mg^{2+}	-3.678	-3.368	-2.654
	$MgHPO_4$		-6.68	-5.657
	$MgH_2PO_4^+$		-6.945	-5.813
	NO_3^-	-3.891	-3.590	-2.891
	Na^+	-4.407	-4.205	-3.776
	$H_2PO_4^-$	-5.288	-4.981	-4.299
	HPO_4^{2-}	-6.134	-5.959	-5.576

The calculated leaching losses are nil when moisture content is 0.1 and 0.5 kg kg^{-1} dry soil; namely the soil holds all water. When moisture content is 1.0 kg kg^{-1} dry soil, water is transported to the underlying soil layer until water content in the top layer is 0.5 kg kg^{-1} dry soil (0.3 * 10^6 kg ha^{-1} water will leach when dry weight of the top layer equals 0.6 * 10^6 kg ha^{-1}). Using the NO_3 and Ca concentrations in liquid phase as calculated with the soil chemical model, the estimated loss of NO_3 and Ca will equal 3.6 and 6.4 kg ha^{-1}, respectively.

This example shows that the combined use of $CaCl_2$ extraction procedure, a soil chemical model and a hydraulic model may estimate nutrient distribution, nutrient speciation and nutrient losses under varying soil moisture conditions.

10.4 Conclusions

Nutrient management in agricultural farms has to change to comply with the increasing demands and boundary conditions of market, society and industry which become more and more strict. Nutrient management decision-making must integrate these demands and must optimize manure and fertilizer applications towards maximal profit, within boundary conditions.

The sensitivity analyses have made clear that the combined use of the standardized $CaCl_2$ procedure and a soil chemical model form a sound basis for a better understanding of nutrient speciation and distribution during $CaCl_2$ extraction and under field conditions. At this moment the extended use of the $CaCl_2$ procedure and the soil chemical model is hindered because relevant soil input characteristics, e.g. quantity and characteristics of the adsorption sites, content of oxides, formation constants, solubility products etc, are not or not readily available. The determination of these characteristics needs further study.

The proposed framework for nutrient management is based on a mechanistic understanding of the soil-plant-nutrient relationships. A soil chemical, soil hydraulic, soil microbial and crop growth model are linked to judge the actual nutrient status and to calculate future status. An important innovative aspect of the framework is that the multi-nutrient 0.01 M $CaCl_2$ soil extraction method is used as a standard method to equilibrate the solid and liquid phase of a soil sample. Subsequently, the composition

of the liquid phase is measured via standard procedures and used as input in asoil chemical model. This input together with additional information on characteristics of e.g the solid phase makes that the soil chemical model can execute the desired calculations. The examples have shown that the perspectives of using the framework for improvement of nutrient management are promising.

Precision agriculture and real-time simulation are helpful concepts in optimizing nutrient management. Integration and combination of the proposed framework of nutrient management decision-making in precision agriculture and real-time simulation is possible. Such integration may lead to an acceleration of the introduction and implementation of good nutrient management on agricultural farms.
The effects of the MINAS policy of the Dutch government on nutrient management in agriculture indicate that the introduction and implementation of adjusted nutrient management has high priority.

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SUMMARY

SUMMARY

Introduction

Farm management is governed by a continuous process of decision-making on strategic, tactical and operational levels, so as to comply with legislation and demands of market, industry and society. In this process, economical, environmental, legislative, agricultural and farm specific boundary conditions have to be integrated and profits optimized. Such decision-making is only possible when data of the actual status of soil, plant, farm economics, etc. are readily available, and when practical tools are available to evaluate the present status and to predict the future status after execution of farm activities.

Nutrient management is a major topic in farm management for various reasons. It determines crop yield and crop quality (i.e. financial crop yield), surpluses of nutrients may result in nutrient losses to the environment, and fertilizer costs contribute to the total farm production costs. It is postulated that the value of current soil and plant testing programs in nutrient management is limited, since most programs are based on 'trial and error' methods and lack a mechanistic underpinning in terms of relevant soil-plant-nutrient relationships. Moreover, most programs are single nutrient programs.

Aim of the thesis was to improve the understanding of the (bio)availability of nutrients in soil to agricultural crops and, thereby, to improve the decision-making process in nutrient management of crop production systems. The specific objectives were as follows:

- to test and improve 0.01 M $CaCl_2$ as multi-nutrient soil extractant in soil testing programs;
- to provide a sound mechanistic interpretation of the results of the multi-nutrient soil extractant 0.01 M $CaCl_2$;
- to develop a conceptual framework that links results of the multi-nutrient soil extractant mechanistically to nutrient demand of crops.

Detailed studies

Eight detailed studies are presented in Chapters 2-9 which increases the understanding of the basic mechanisms that occur during the extraction of nutrients from soil with $CaCl_2$. The perspectives of the design of a multi-nutrient 0.01 M $CaCl_2$ soil testing program is evaluated. Much attention has been paid in the studies to the nutrients Ca, Mg and K. The results of the detailed studies were the basis for the set up of a conceptual framework for nutrient management decision-making (Chapter 10).

Literature is reviewed on the perspectives of current soil and plant testing programs as a tool for optimization of fertilization strategies (Chapter 2). Most of the current programs turn out to be single nutrient programs, are site specific and focus on maximal crop production or maximal financial crop yield and do not take environmental considerations into account. The analytical procedures in the programs are labour intensive and time-consuming. Data are not readily available and its reliability some times questionable. The fertilizer recommendations in the programs are deduced from 'trial and error' methods and lack a mechanistic underpinning in terms of relevant soil-plant-nutrient relationships. Present day computer technology is seldom used to refine, optimize or develop more dynamic fertilizer recommendations. It is concluded that most of the current soil and plant testing programs are not a valuable tool for nutrient management.

Economical and operational aspects of 0.01 M $CaCl_2$ as a multi-nutrient soil extractant make the procedure attractive for the development of a 0.01 M $CaCl_2$ soil testing program. A literature review has been carried out on the soil chemical, analytical and plant nutritional aspects of $CaCl_2$ solutions as a soil extractant (Chapter 3). $CaCl_2$ solutions are often used as a single nutrient extractant and the amount of plant nutrient extracted turns out to be sensitive for differences in sample treatment and extraction procedure. Therefore, the 0.01 M $CaCl_2$ soil extraction procedure must be standardized. Calibration studies show reasonable relationships between nutrient elements extracted by the 0.01 M $CaCl_2$ procedure and conventional procedures. It is concluded that a 0.01 M $CaCl_2$ soil testing program is a promising tool for optimization of nutrient management.

In the current soil drying protocol of the 0.01 M $CaCl_2$ procedure, soils are oven dried at 40°C for 24h. From literature it is well known that soil drying may affect the amount of nutrient element extracted compared to moist soils. Chapter 4 gives the results of an explanatory study in which the effect was determined of oven drying temperature and forced-air ventilation on pH and the amount of soluble organic N (org-N), NH_4-N, NO_3-N, *ortho*-P, K, Mg, Na and Mn extracted by 0.01 M $CaCl_2$. Increasing drying temperature and the use of forced air ventilation affected pH and most of the nutrient elements extracted. Mg was not affected by drying temperature and at 20° and 40°C not affected by forced air ventilation. There was no effect of forced air ventilation on K extracted but the effect of drying temperature was variable. Based on the differences found between moist and dried soils for pH and for nutrients, it is questionable whether soil drying should be recommended in the 0.01 M $CaCl_2$ procedure. If soil drying is preferable because of sample storage or optimization of laboratory activities, drying temperature should not exceed 40°C.

A simple straightforward conversion of conventional soil testing programs into a 0.01 M $CaCl_2$ soil testing program has been suggested by using the relationship between test values of the 0.01 M $CaCl_2$ extractant and those of conventional extractants. However, these relationships are often weak and an interpretation of the coefficient(s) of the regression equations is questionable. Therefore, a fundamental relationship has been deduced relating magnesium (Mg) extracted by conventional methods with Mg extracted from dried soils by the 0.01 M $CaCl_2$ method (Chapter 5). The coefficients in the relationship are related to characteristics of the extraction procedure and Mg fractions in the soil. The magnitude of the actual cation exchange capacity (actual CEC) of the soil during $CaCl_2$ extraction is an important explaining variable. The relationship has been tested for seven conventional Mg extractants. For six conventional extractants the explained variance was more than 0.92. We concluded that the derived fundamental relationship could be used for the design of a more mechanistically based $CaCl_2$ soil testing program for Mg. It is stated that the fundamental relationship can also be used for the design of a $CaCl_2$ soil testing program for potassium (K).

The actual cation exchange capacity (CEC) of the soil during $CaCl_2$ extraction is an important explaining variable in the relationship between Mg extracted by 0.01 M $CaCl_2$ and six conventional Mg extractants (Chapter 5). However, determination of the actual CEC necessitates an extra analytical procedure. In Chapter 6 a procedure is tested for the estimation of the actual CEC of a soil. The study showed that the actual CEC could be calculated as the summation of the charge of organic carbon and clay at the actual pH of the soil. The actual pH equals pH measured in the liquid phase of the soil suspension after the $CaCl_2$ extraction. It was concluded that the proposed procedure could be used for estimation of the actual CEC.

After the 0.01 M $CaCl_2$ procedure, still considerable amounts of exchangeable K and Mg are retained at the soil exchange sites. It suggests that $CaCl_2$-extractable K of Mg does not equal the pool of plant available K or Mg. To test this suggestion, the pool of plant available K was determined via 'soil exhaustion' by maize and tomato using the double pot technique (Chapter 7). Dry matter production and K uptake showed a moderate relationship with $CaCl_2$-extractable K. However, dry matter production showed a good relationship with K extracted by the unbuffered 0.01 M $BaCl_2$ method. The amount of $BaCl_2$-extractable K equalled the pool of plant available K in soils with less than 20% clay. In soils with more than 20% clay, K uptake exceeded $BaCl_2$-extractable K. It is suggested that K is released from clay particles at clay contents exceeding 20%.

The unbuffered 0.01 M $BaCl_2$ method extracts exchangeable cations. A method has been derived (Chapter 8) to calculate the amount of exchangeable soil Mg and K and the amount of Mg and K retained at the soil exchange sites after $CaCl_2$ extraction. In this method the selectivity coefficients of the Ca-Mg, Ca-K and Mg-K exchange reactions during the $CaCl_2$ procedure are important input variables. These coefficients have been determined for neutral, non-sodic soils (Chapter 8). The coefficients are related to one or more of the following soil characteristics: % organic C, the ratio of cations in the filtrate after $CaCl_2$ extraction, the fraction of the total negative charge originating from clay and % clay. Generally, these characteristics are well known or can be estimated easily. It is concluded that the amount of Ca, Mg and K retained at the soil exchange sites can be calculated using the Ca, Mg and K concentrations of the

filtrate after 0.01 M $CaCl_2$ extraction, the deduced selectivity coefficients and the actual CEC (see Chapter 6).

During the derivation of the selectivity coefficients it turned out that the total positive charge of cations extracted by the unbuffered 0.01 M $BaCl_2$ method (ISO 11260) did not equal the total negative charge of the actual CEC measured via the same method. A study was carried out to determine the backgrounds of this difference (Chapter 9). It was shown that the unbuffered $BaCl_2$ method (ISO 11260) underestimates the actual CEC for soils high in CEC and, therefore, it is recommended that the ISO procedure should be adjusted.

Framework for nutrient management and conclusions

In Chapter 10 the results of the studies were integrated. A conceptual framework for a mechanistic approach of the soil-plant-nutrient relationships in nutrient management has been worked out. Three steps can be distinguished in the concept. In the first step the multi-nutrient 0.01 M $CaCl_2$ soil extraction procedure is used as a standardized procedure to give a chemical characterization of soils at a pH and ionic strength comparable to field conditions. In the second step a soil chemical model, crop growth model, microbiological model and soil hydraulic model are combined and integrated. The four models are linked and are the basis for a mechanistic approach of the soil-plant-nutrient relationships in agricultural soils. In the soil chemical model the results of the $CaCl_2$ soil extraction are used as input parameter. Nutrient speciation and nutrient distribution for different $CaCl_2$ extraction conditions or under different soil field conditions can then be calculated. The pool of plant available nutrients is an important growth-determining factor in crop growth. The nutrient speciation and distribution as calculated in step 2 can be used to define this pool. In the third step, step 2 is coupled to an optimization procedure which optimizes fertilization and nutrient management to the demands on farm profitability, plant growth, soil nutrient status, crop production and crop quality and legislative and environmental boundary conditions.

The innovative aspects in the proposed concept are:

- the use of the $CaCl_2$ soil extraction procedure to standardize the equilibration of the liquid and solid phase of the soil under study (step 1);
- the use of $CaCl_2$ soil extraction data in a soil chemical model and the calculation of nutrient speciation and distribution with this model (step 2);
- the use of the calculated nutrient speciation and distribution in a crop growth model (step 2); and,
- the use of an optimization procedure to optimize nutrient managament taking into account farm specific and agricultural demands and legislative and environmental boundary conditions (step 3).

The building blocks of the framework, i.e. the 0.01 M $CaCl_2$ procedure, a soil chemical model, a crop growth model, a soil microbiological model, a soil hydraulic model and an optimization procedures, are available but need to be integrated into a computer model.

The studies presented in this thesis have increased the understanding of the availability of nutrients in soil to agricultural crops. The 0.01 M $CaCl_2$ reagent turned out to be a promising multi-nutrient soil extractant. A sound mechanistic interpretation of the 0.01 M $CaCl_2$ soil extraction results is possible. A conceptual framework for nutrient management decision-making has been developed which links results of the multi-nutrient soil extractant mechanistically to nutrient requirements of crops. The design of a multi-nutrient 0.01 M $CaCl_2$ soil testing program is possible but requires more research.

SAMENVATTING

SAMENVATTING

Inleiding

In de bedrijfsvoering van landbouwbedrijven worden vrijwel continue beslissingen genomen op strategisch, tactisch en operationeel managementniveau om te kunnen voldoen aan regelgeving en eisen van de maatschappij en industrie. In dit beslisproces worden economische, milieukundige, wettelijke, landbouwkundige en bedrijfsspecifieke randvoorwaarden geïntegreerd en geoptimaliseerd naar een (maximaal) bedrijfsresultaat. Zo'n beslisproces is alleen maar mogelijk als gegevens over de actuele toestand van bodem, gewas, financiële situatie van het bedrijf, etc. makkelijk beschikbaar zijn, en wanneer hulpmiddelen ter beschikking staan om de actuele toestand te evalueren en om de toekomstige toestand te schatten na uitvoering van landbouwkundige handelingen of na zich veranderende groeiomstandigheden.
Nutriëntenmanagement is een van de belangrijkste thema's in de bedrijfsvoering van landbouwbedrijven. Nutriëntenmanagement, en met name de uitgevoerde bemesting daarin, bepaalt mede de gewasopbrengst en –kwaliteit (en daarmee de financiële gewasopbrengst). Een te hoge bemesting kan leiden tot ongewenste neveneffecten op het milieu. Voor de productie van meststoffen worden eindige voorraden grondstoffen gebruikt en de bemestingskosten zijn een wezenlijk onderdeel van de totale productiekosten van bedrijven. De waarde van het huidige grond- en gewasonderzoek als basis voor de gewenste, snelle en adequate aanpassingen in nutriënten-management lijkt beperkt (Hoofdstuk 2).

Doel van dit proefschrift is bij te dragen aan het begrip van (bio-)beschikbaarheid van nutriënten in de bodem voor gewassen om daarmee het beslisproces omtrent nutriëntenmanagement te verbeteren. De specifieke doelen van dit proefschrift zijn als volgt:

- het testen en verbeteren van 0,01 M $CaCl_2$ als een multi-nutriënt grondextractiemiddel;
- te komen tot een mechanistische interpretatie van de resultaten van de 0.01 M $CaCl_2$ extractieprocedure;

- een conceptueel raamwerk te ontwikkelen waarmee resultaten van 0.01 M $CaCl_2$ als multi-nutriënt grondextractiemiddel op een mechanistische wijze worden gekoppeld aan de nutriëntenbehoefte van gewassen.

Gedetailleerde onderzoeken

Als eerste stap is een literatuuronderzoek uitgevoerd naar de perspectieven van het gebruik van de huidige grond- en gewasonderzoekprogramma's als hulpmiddel voor de optimalisatie van bemestingsstrategieën (Hoofdstuk 2). De meeste van de huidige programma's blijken zich te beperken tot één nutrient, zijn vaak locatiespecifiek en richten zich enkel op een maximale gewasproductie en maximale financiële gewasopbrengst. De analytische procedures en handelingen op het laboratorium zijn arbeidsintensief en tijdrovend en daardoor zijn data niet snel beschikbaar en is de betrouwbaarheid soms twijfelachtig. De bemestingsadviezen in de programma's zijn veelal afgeleid met behulp van empirische 'trial and error' methoden. Er ontbreekt een mechanistische onderbouwing in termen van relevante, wetenschappelijke bodem-plant-nutriënt relaties. De hedendaagse computertechnologie wordt niet of zelden gebruikt om bestaande adviezen te verfijnen c.q. te optimaliseren of om meer dynamische adviezen te ontwikkelen. Er is geconcludeerd dat de huidige grond- en gewasonderzoeksprogramma's niet goed bruikbaar zijn voor de verdere optimalisatie van bemestingsstrategieën.

Economische en operationele aspecten van een 0,01 M $CaCl_2$ oplossing als een multi-nutriënt grondextractiemiddel maakt het aantrekkelijk om de 0,01M $CaCl_2$ grondextractieprocedure te gebruiken voor de ontwikkeling van een 0,01 M $CaCl_2$ grondonderzoeksprogramma. Er is een literatuuronderzoek uitgevoerd naar bodemchemische, analytische en plantenvoedings aspecten van het gebruik van $CaCl_2$ als grondextractiemiddel (Hoofdstuk 3). $CaCl_2$-oplossingen worden vaak gebruikt voor de extractie van een enkel nutriënt. De hoeveelheid geëxtraheerd nutriënt blijkt gevoelig te zijn voor monstervoorbehandeling en extractieprocedure. Daarom moet de 0,01 M $CaCl_2$ procedure gestandaardiseerd worden. Er bestaat een redelijke relatie tussen de hoeveelheid nutriënt geëxtraheerd met de 0,01 M $CaCl_2$ procedure en die met conventionele procedures. Er is geconcludeerd dat de 0,01 M $CaCl_2$ procedure een

veelbelovend hulpmiddel is om te komen tot een meer mechanistische benadering van nutriëntenmanagement.

In het huidige protocol voor het drogen van grond in de 0,01 M $CaCl_2$ procedure staat beschreven dat gronden moeten worden gedroogd gedurende 24 uur bij 40°C. Het is in de literatuur bekend dat het drogen van grond invloed heeft op de hoeveelheid nutriënt die wordt geëxtraheerd. Hoofdstuk 4 geeft de resultaten weer van een onderzoek naar het effect van oventemperatuur en geforceerde beluchting op de pH en de hoeveelheden oplosbare organische N (org-N), NH_4-N, NO_3-N, *ortho*-P, K, Mg, Na en Mn die worden geëxtraheerd uit grond na extractie met 0,01 M $CaCl_2$. Verhoging van de oventemperatuur en het gebruik van geforceerde beluchting had invloed op de pH en bij de meeste nutriënten invloed op de hoeveelheid geëxtraheerd nutriënt. De hoeveelheid geëxtraheerd Mg was onafhankelijk van oventemperatuur en werd bij 20° en 40°C niet beïnvloed door de geforceerde beluchting. Er was geen effect van een geforceerde beluchting op de hoeveelheid geëxtraheerde K terwijl het effect van oventemperatuur op de hoeveelheid geëxtraheerde K variabel was. Gelet op de verschillen die zijn vastgesteld tussen gedroogde en niet-gedroogde grond, is het twijfelachtig of in de $CaCl_2$ procedure geadviseerd zou moeten worden om grond te drogen. Als toch wordt gedroogd, dan zou de temperatuur niet hoger mogen zijn dan 40°C.

De omzetting van conventionele grondonderzoeksprogramma's in een $CaCl_2$ grondonderzoekprogramma zou kunnen plaatsvinden op basis van de relatie tussen de hoeveelheid nutriënt geëxtraheerd met de $CaCl_2$ procedure en die met conventionele procedures. Deze relaties zijn echter vaak matig en er is geen of een beperkte mechanistische interpretatie mogelijk van de coëfficiënten in de regressievergelijkingen. Voor Mg is een mechanistische basisrelatie afgeleid tussen Mg geëxtraheerd volgens conventionele methoden en Mg geëxtraheerd met de $CaCl_2$ procedure (Hoofdstuk 5). De coëfficiënten in de relatie zijn gerelateerd aan Mg-fracties in de bodem en karakteristieken van de extractieprocedure. De grootte van de actuele CEC van de grond tijdens de $CaCl_2$ procedure blijkt een belangrijke verklarende variabele te zijn. De basisrelatie is getest voor zeven conventionele Mg extractiemiddelen. Bij zes extractiemiddelen was de verklaarde variantie meer dan

0.92. Er is geconcludeerd dat de basisrelatie bruikbaar is om te komen tot een ontwerp van een $CaCl_2$ grondonderzoekprogramma voor Mg. De basisrelatie lijkt ook bruikbaar te zijn voor K.

De actuele CEC van een grond tijdens de $CaCl_2$ extractie is een belangrijke verklarende variabele in de relatie tussen Mg geëxtraheerd met $CaCl_2$ en Mg geëxtraheerd met conventionele Mg extractiemiddelen (Hoofdstuk 5). Echter de bepaling van de actuele CEC vraagt een extra analytische bepaling.

In Hoofdstuk 6 wordt een procedure getest voor het schatten van de actuele CEC van gronden. Uit de studie blijkt dat de actuele CEC berekend kan worden als de som van de lading van de organische koolstof en kleimineralen bij de actuele pH van de bodem. De actuele pH is hierbij gelijk aan de pH gemeten in de vloeistoffase van de bodemsuspensie bij de 0,01 M $CaCl_2$ extractie. Er is geconcludeerd dat de voorgestelde methode bruikbaar is om de actuele CEC te schatten.

Bij de 0,01 M $CaCl_2$ procedure blijft nog een aanzienlijke hoeveelheid omwisselbare K en Mg achter op de omwisselplaatsen van de bodem. Het suggereert dat de hoeveelheid $CaCl_2$ extraheerbaar K of Mg niet gelijk is aan de voorraad plantbeschikbare K en Mg in de bodem. Om dit te testen is de voorraad plantbeschikbaar K in gronden bepaald door uitputting van de gronden met maïs en tomaten. Daarbij is gebruik gemaakt van de dubbele-pottechniek (Hoofdstuk 7). De drogestofproductie en de K-opname vertoonden een matige relatie met de hoeveelheid K die werd geëxtraheerd met $CaCl_2$. Echter, de drogestofproductie vertoonde een goede relatie met de hoeveelheid K geëxtraheerd via de niet-gebufferde 0,01 M $BaCl_2$ methode. In gronden met minder dan 20% klei kwam de hoeveelheid $BaCl_2$ extraheerbaar K overeen met de voorraad plantbeschikbare K. In gronden met meer dan 20% klei was de K-opname groter dan de hoeveelheid $BaCl_2$ extraheerbaar K. De resultaten suggereren dat in deze gronden K vrijkomt uit kleimineralen.

De niet-gebufferde 0,01 M $BaCl_2$ extraheert omwisselbare kationen uit een grond. Er is een methode afgeleid (Hoofdstuk 8) waarmee de totale hoeveelheden omwisselbare K en Mg in een bodem en de hoeveelheden K en Mg die achterblijven aan het omwisselcomplex na $CaCl_2$ extractie, kunnen worden berekend. In deze methode zijn de selectiviteitscoëfficiënten van de Ca-Mg, Ca-K en Mg-K omwisselreacties tijdens

de 0,01 M $CaCl_2$ procedure belangrijke inputvariabelen. Deze coëfficiënten zijn bepaald voor neutrale, niet-zoute gronden (Hoofdstuk 8). De coëfficiënten zijn gerelateerd aan % organische koolstof, de ratio van kationen in het filtraat na de $CaCl_2$ extractie, de fractionele bijdrage van kleimineralen aan de totale negatieve lading van een grond en het percentage klei. Deze karakteristieken zijn in het algemeen bekend of kunnen makkelijk geschat worden. Er is geconcludeerd dat de hoeveelheden Ca, Mg en K die achterblijven aan het omwisselcomplex na $CaCl_2$ extractie, berekend kunnen worden met behulp van gegevens over de samenstelling van het filtraat na de $CaCl_2$ extractie, de afgeleide selectiviteitscoëfficiënten en de actuele CEC van de gronden.
Bij de afleiding van selectiviteitscoëfficiënten bleek dat de totale positieve lading van kationen, die werden geëxtraheerd met de niet-gebufferde 0,01 M $BaCl_2$ methode (ISO 11260), niet gelijk was aan de totale negatieve lading van de actuele CEC die met dezelfde methode werd gemeten. Er is een studie uitgevoerd naar de oorzaak van dit verschil (Hoofdstuk 9). Er is aangetoond dat de niet-gebufferde $BaCl_2$ methode de actuele CEC onderschat voor gronden met een grote CEC. Er is geadviseerd om de ISO-procedure van de niet-gebufferde $BaCl_2$ methode aan te passen.

Raamwerk voor nutriëntenmanagement en conclusies

De resultaten van de Hoofdstukken 2 tot en met 9 zijn in Hoofdstuk 10 geïntegreerd en uitgewerkt tot een conceptueel raamwerk voor een mechanistische benadering van bodem-plant-nutriënt relaties in nutriëntenmanagement. In het concept worden drie stappen onderscheiden. In de eerste stap wordt de gestandaardiseerde 0,01 M $CaCl_2$ grondextractieprocedure gebruikt om te komen tot een chemische karakterisering van gronden bij een pH en ionsterkte vergelijkbaar met die onder veldomstandigheden. In de tweede stap worden een bodemchemisch model, een gewasgroeimodel, een microbiologisch model en een bodemfysisch model gecombineerd en geïntegreerd. De vier modellen werken simultaan en vormen de basis voor een meer mechanistische benadering van bodem-plant-nutriënt relaties in landbouwgronden. Het bodemchemisch model gebruikt de gegevens van de $CaCl_2$ grondextractieprocedure als inputparameter. Het bodemchemisch model kan de speciatie en verdeling van nutriënten ook berekenen bij een afwijkende uitvoering van de $CaCl_2$ procedure en/of

bij afwijkende veldomstandigheden. De voorraad plantbeschikbaar nutriënt in een bodem is een belangrijke groei-bepalende factor voor gewassen. De speciatie en verdeling van nutriënten zoals berekend in stap 2 kan gebruikt worden om deze voorraad te definiëren. In stap 3 wordt stap 2 gekoppeld aan een optimalisatie procedure die bemesting en nutriëntenmanagement optimaliseert, rekening houdend met eisen met betrekking tot winstgevendheid, gewasgroei, bodemvruchtbaarheid, gewasproductie en –kwaliteit en met wettelijke en milieukundige randvoorwaarden. De innovatieve aspecten van het voorgestelde concept zijn:

- het gebruik van de $CaCl_2$ grondextractieprocedure om de evenwichtsinstelling tussen de vloeibare en vaste fase van gronden te standaardiseren (stap 1);
- het gebruik van resultaten van de $CaCl_2$ grondextractie in een bodemchemisch rekenmodel en de berekening van de speciatie en verdeling van nutriënten in een grond met een bodemchemisch model (stap 2);
- het gebruik van de berekende speciatie en verdeling van nutriënten in een gewasgroeimodel (stap 3); en,
- het gebruik van een optimalisatieprocedure om nutriëntenmanagement te optimaliseren rekening houdend met bedrijfsspecifieke, landbouwkundige, wettelijke en milieukundige randvoorwaarden (stap 3).

De bouwstenen, dat wil zeggen de 0.01 M $CaCl_2$ procedure, het bodemchemisch rekenmodel, het gewasgroeimodel, het microbiologisch model, het bodemfysisch model en de optimalisatieprocedure, zijn beschikbaar maar moeten nog wel geïntegreerd worden in een computermodel en vervolgens getoetst worden in de praktijk.

De studies die in dit proefschrift zijn gepresenteerd, hebben het begrip omtrent de beschikbaarheid van nutriënten in de bodem voor planten vergroot. Een 0,01 M $CaCl_2$ oplossing is een veelbelovend multi-nutriënt grondextractiemiddel.. Het was mogelijk de resultaten van de $CaCl_2$ procedure te verklaren met behulp van een mechanistische benadering. Het conceptueel raamwerk voor een nutriëntenmanagement beslisproces, waarin via een mechanistische benadering de resultaten van een 0,01 M $CaCl_2$ grond extractie worden gekoppeld aan de nutriëntenbehoefte van gewassen, biedt

perspectieven voor een verdere ontwikkeling. De verdere ontwikkeling van een multi-nutriënt $CaCl_2$ grondonderzoekprogramma vraagt nog wel veel onderzoektijd.

CURRICULUM VITAE

Peter (Petrus Johannes) van Erp werd geboren op 9 juli 1958 te Vught (NBr.) Na de middelbare school volgde hij de Hogere Tuinbouw School te 's-Hertogenbosch waar hij in 1980 het einddiploma behaalde. Direct daarna begon hij de studie Bodemkunde en Bemestingsleer (N33) aan de Landbouw Hogeschool te Wageningen. In 1985 rondde hij deze studie cum laude af met als afstudeervakken Bodemvruchtbaarheid en Plantenvoeding, Bodemscheikunde, Kolloïdchemie en Pedagogiek en Algemene Didactiek.

In de periode 1985 tot 1988 was hij in dienst als onderzoeker bij het toenmalige Instituut voor Bodemvruchtbaarheid (IB) te Haren. Hij deed daar onderzoek naar de landbouwkundige waarde van organische afvalstoffen en de invloed van zware metalen daarop. In dezelfde periode was hij parttime docent aan het Prof. Van Hall Instituut te Groningen. Hij doceerde daar de vakken scheikunde en bodemverontreiniging en begeleidde studenten bij het afstuderen.

In de periode 1988 tot 2001 was hij in dienst van het Nutriënten Management Instituut NMI. In de periode van 1988 tot medio 1993 was hij gedetacheerd bij het toenmalige Instituut voor Bodemvruchtbaarheid en van 1993 tot 2000 bij de vakgroep Bodemkunde en Plantenvoeding van de Landbouwuniversiteit te Wageningen. Vanaf 2000 tot 2001 werkte hij op het NMI-hoofdkantoor te Wageningen. In de periode van 1988 tot 2001 deed hij onderzoek aan en was betrokken bij de vele facetten van het onderzoek aan bodem-plant-nutriënt relaties; eerst als onderzoeker maar vanaf 1994 als hoofd onderzoek. Tijdens de periode van detachering bij de vakgroep Bodemkunde en Plantenvoeding raakte hij betrokken bij onderzoek waarin de mogelijkheden van 0,01 M $CaCl_2$ als universeel grondextractiemiddel werden onderzocht. De resultaten die in het kader van dit onderzoek door de vakgroep werden verzameld, vormden de basis voor het voor U liggende proefschrift.

Vanaf medio 2001 is hij werkzaam bij PPO (Praktijkonderzoek Plant en Omgeving) als teamleider bij het team Paddestoelen te Horst (toenmalig Proefstation voor de Champignoncultuur). Hij is daar verantwoordelijk voor onderzoeksinhoudelijke en locatiespecifieke managementzaken van het team.