

COMPATIBILITY OF SOIL ANALYTICAL DATA

Determinations of Cation Exchange Capacity, Organic Carbon,
Soil Reaction, Bulk Density, and Volume percent of water at
selected pF values by different methods

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INTERNATIONAL SOIL REFERENCE AND INFORMATION CENTRE

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EXTENDED SUMMARY

Introduction

In april 1993 the IGBP-DIS working group members insisted on a preprocessing of the data (homogenization) before entering them into a general purpose database. A transfer facility necessary to test this homogenization on pedons of USDA-SCS, FAO and ISRIC is currently under development at ISRIC and can be used to meet their requirements.

Serious problems arise with the comparison of analytical data stored within different datasets. Soil analyses are very often carried out by different methods, sometimes even not specified within a database. The key question is if the method for determining a soil attribute does or does not influence the result.

A study reviewing the possibilities and limitations of soil analytical methods with regard to the compatibility of the results obtained was carried out. A limited amount of literature and experts on analytical procedures were consulted. The list of attributes studied coincides with those selected by the IGBP-DIS working group members at Silsoe, October 1992. Emphasis was laid on the determinations of cation exchange capacity, organic carbon, soil reaction, bulk density and volume percent of water at selected pF values.

General results

A comparison of results determined by different methods shows that conversion of data can be accomplished in two ways. By merely adding or subtracting the average difference between methods and by using appropriate regression equations. The latter are more accurate but are found only occasionally for specified soil types and for a limited number of methods.

The International Organization for Standardization (ISO) is trying to achieve uniformity on analytical methods. Nevertheless experiences show that even when analytical methods are standardized a certain minimum level of variation will appear to be unavoidable (Van Reeuwijk, 1982). For some pedologists this variation, at least for some soil attributes, will be acceptable.

For the purpose of discussion it might be useful to subdivide laboratory methods into two main groups:

- a) analysis focused on the general characterisation of the soil.
- b) analysis which can provide indexes of nutrient availability.

Examples of the first group are pH, organic carbon and EC. Examples of the second group are available phosphorus, nitrogen and potassium. Attributes obtained by analytical methods of the first group can usually be defined quite clearly, and rather satisfactory methods are available to get an impression of the potential qualities of a soil. Lack of true understanding of the processes governing the availability of nutrients has led to the development of an ever-increasing number of methods falling into the second group, each claiming preference for use under specified conditions (Houba *et al.*, 1988). The results from the first group of laboratory methods are therefore easier to compare than the results from the second group.

Cation Exchange Capacity

The Cation Exchange Capacity as a function of the specific surface of the soil and the electrical charge on the soil particle surface, can be satisfactorily analyzed for soils of the temperate regions by extraction solutions at some specified pH value.

For many tropical soils dominated by a variable charge, there is a change in surface charge and hence CEC, with pH and ionic strength of the soil solution. Therefore the character of the extraction solution affects the result which makes CEC data almost incompatible.

Soil Taxonomy (1975) and Fenger *et al.* (1986) present more than one CEC value for identical soil samples, each of them determined by a different method. By way of regression analysis it has been possible to estimate the CEC value of a certain method from experimental information obtained by another method. In order to prevent misinterpretations and even improper use of regression equations the prediction interval of a future observed response has been determined for a group of Inceptisols from the USA and Mollisols from Tanzania for which correlations (r^2) of 0.9 and 0.5 were observed.

It will be useful to determine the influence of pH and Organic Carbon content as independent variables on the CEC values, generating more complex relations than the linear ones studied until now. Next it is recommended to repeat the exercise of obtaining CEC data by different methods from soils of other climatic regions.

Organic Carbon

Carbon values determined by means of the dry combustion method as well as the direct wet combustion methods appear to be comparable because they are able to recover 100% of the organic C. Indirect wet combustion methods like Kurmies, Tinsley and Mebius are able to recover most of the organic C and the results of these methods are comparable with results obtained by dry combustion or direct wet combustion.

The original Walkley-Black method however provides a variable recovery of organic C from soils and the correction or recovery factor used to convert the C-value determined to the total C, varies greatly from one soil to another. Results obtained by this method give therefore an approximation of organic C in soils and they are difficult to compare with results from other methods.

Bulk Density

For most soils the core sampling method is generally taken to be the standard method, although the method is somewhat unsatisfactory for stony or noncoherent samples. Bulk density values determined by this method are comparable with values obtained by the clod method, which measures displacement of water.

Other less common methods like the sand replacement method, the auger-hole method and the modified clod method which measures displacement of mercury or kerosene instead of water, yield in most cases bulk density values which deviate only a few percent from the values obtained by the core method.

Indirect methods making use of the scattering or transmission of nuclear radiation by soil, yield density values which do not differ much from values determined by different direct methods. However soils with a very specific composition, like gravelly soils or peaty soils yield unacceptable large differences.

Soil Reaction

pH values measured in water increase in some cases with the dilution of the suspension. The increase is however not proportional and is sometimes not observed. The pH values of a saturated paste are always lower than the values measured in a soil/water solution, because of less dilution and higher H-ion concentrations.

For temperate soils, and many tropical ones 0.01M CaCl₂ suspensions are often used. Measuring pH in a KCl suspension is particularly applicable to acidic, highly weathered soils dominated by colloids with variable surface charge characteristics. The soil pH of both mineral and organic soils, determined by using water is normally 0.5 to 1.5 units higher than pH values measured in diluted solutions of CaCl₂ and KCl, respectively. pH values for non calcareous soils, measured in CaCl₂ or KCl are almost equal and virtually independent of the soil-solution ratios used.

Volume percent of water at selected pF values

Few references can be found in the literature which compare different methods to determine water retention values. The reason for this is that each method is used for a different range of suctions, in order to bring a soil into equilibrium with a defined tension followed by the determination of the moisture content by weight.

Conclusions

Analytical methods have been reviewed which indicate that methods for organic carbon, bulk density and to a certain extent soil reaction (pH) yield comparable and interchangeable results. Methods to determine cation exchange capacity (CEC) are very different and soil dependent giving results which are incompatible.

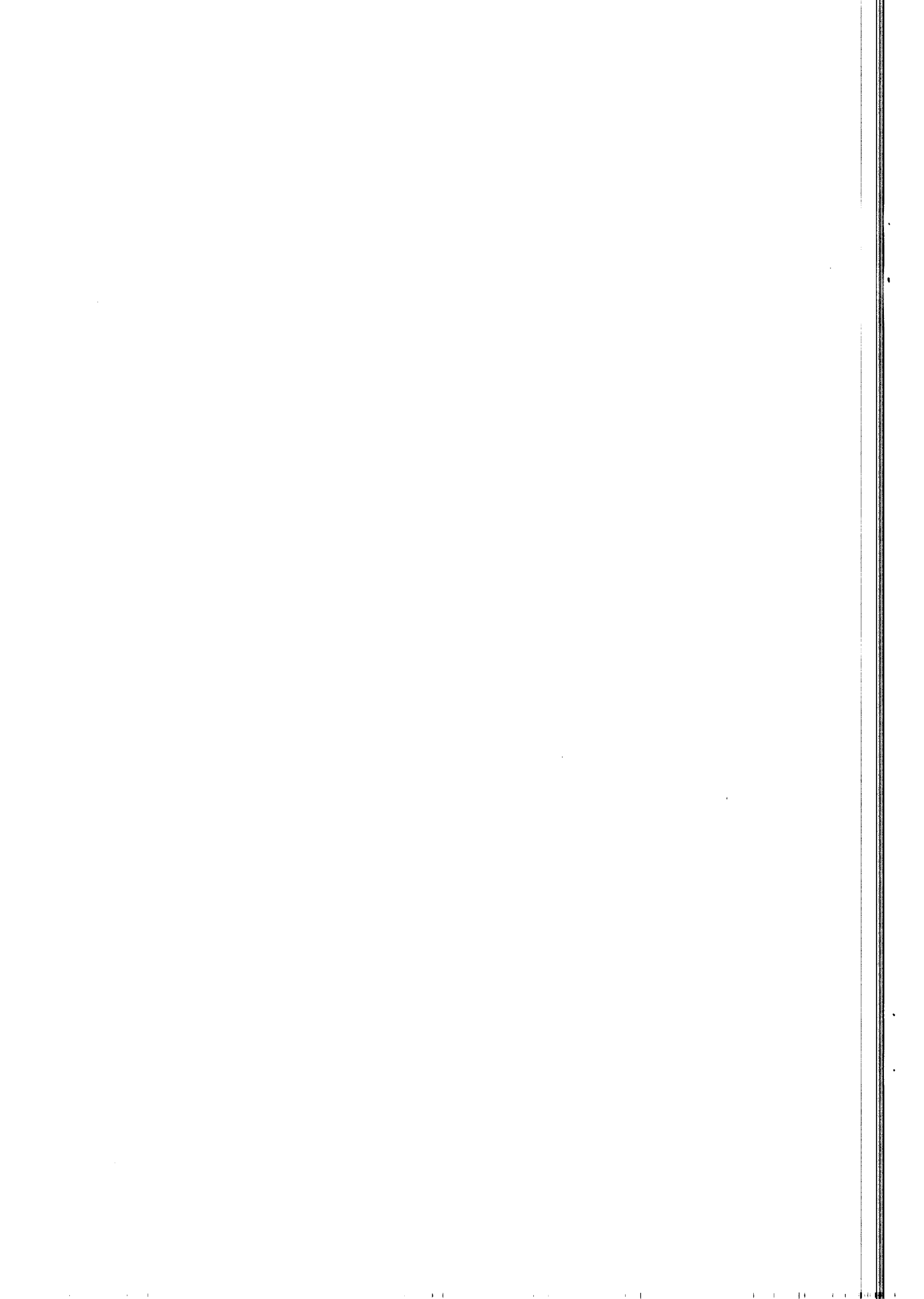
It will be worthwhile to compare the relative importance of spatial variability (variation of attribute values for a specific group of soil pedons, e.g. belonging to one classification unit in a particular climatic zone) versus variations caused by different analytical methods.

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1 INTRODUCTION

At a meeting in January 1993, representatives from USDA-SCS, ISRIC, FAO, ORSTOM, the UK Silsoe group and members of the International Geosphere and Biosphere Programme - Data and Information System (IGBP-DIS) office agreed that a methodology should be developed which permits the linking of disparate existing data sets. Bringing the datasets together will go a considerable way towards a world dataset indispensable for global change research. The next step will be to include other data sets as they become available.

In april 1993 the IGBP-DIS working group members insisted on a preprocessing of the data (homogenization) before entering them into a general purpose database. A transfer facility necessary to test this homogenization on pedons of USDA-SCS, FAO and ISRIC is currently under development at ISRIC and can be used to meet their requirements.

During the development of the transfer facility it appeared that for the exchange of all objects and their attributes stored within the databases it is absolutely necessary that a clear conception exists. Only then consistent results in any evaluation and analysis using data from various data sources can be guaranteed (Tempel, 1994 - in press).

One of the basic problems is the evaluation of analytical information obtained in most cases by means of different laboratory methods. In the second Chapter of this report the results are presented of a small study reviewing the possibilities and limits of soil analytical methods with regard to the compatibility of the results obtained. A limited amount of literature and experts on analytical procedures were therefore consulted.

Literature references in which the exact values of soil attributes are presented that have been obtained by way of two or more different methods are rare. An exception might be Soil Taxonomy (1975) and Fenger *et al.* (1986) in which Cation Exchange Capacity data are provided determined by two methods. By way of regression analysis it is possible to observe if there is any relation between the results of both methods. The results are given in Chapter 3 as well as a comparative literature review.

Organic carbon and bulk density are two soil attributes of which many scientists presume that different analytical methods yield the same results and that as a consequence these results are comparable and interchangeable. A literature review was carried out in order to evaluate these ideas of which the results are presented in Chapter 4 and 6 respectively.

Soil reaction (pH) can be determined in a soil:water suspension, while other suspensions such as KCl and CaCl₂ are also employed. Differences between the results of these methods as well as solid:liquid ratios are illustrated in Chapter 5.

Finally in Chapter 7 various methods to determine the volume percent of water at selected pF values are presented as well as a comparison between the results obtained by each of them.

2 ANALYTICAL SOIL DATA DETERMINED BY DIFFERENT METHODS AS STORED IN THE DATA BASES ISIS, FAO-ISRIC SDB, SOTER AND WISE

2.1 Introduction

Serious problems arise with the comparison of analytical data stored in different datasets. Soil analyses are very often carried out by different methods, sometimes even not specified within a database.

At first sight the method for determining the total content of a certain element in a soil sample should have little or no influence on the final results. This, however, is not always the case. Extractable fractions, where the character of the extracting solution and the operation necessary to dissolve an element or the compound that contains it indeed affect the results, are an example of that. Hence the analytical method used is extraordinarily important, and results vary accordingly from one to another. Therefore it is necessary to know the nature of the procedures before making a valid interpretation of soil analysis (Etchevers, 1986) and considering if it is possible to compare and interchange the results of these analysis.

In order to get an idea on the possibilities and limitations of such a comparison and interchange of data an inventory was made by interviewing a small group of experts on laboratory procedures and by reviewing a limited amount of literature. The results are reported in this chapter.

2.2 Chemical and physical attributes in datasets as used by ISRIC

In Annex 1 a review is presented of the analytical information which forms part of the four different datasets used at ISRIC. A comparison between ISIS, FAO-ISRIC SDB, SOTER and WISE database show the following:

- * Within each of the four databases there is some space available to include physical and chemical attributes and to indicate the analytical method used. ISIS by way of additional remarks, the other three datasets by way of codes, whereas WISE and SOTER also offer the possibility to include a descriptive part.
- * Only in the WISE database codes are defined for each of the analytical methods and in practice a systematically use is made of them to store new analytical data and their corresponding methods. The other systems did not define these codes (yet).
- * In the case of the ISIS database the lack of method definition does not necessarily present a big problem as long as the analyses are carried out in a standard way by ISRIC's own laboratory. Analytical methods used by NASREC countries however can be quite different and the results of these analyses cannot be interchanged or directly compared with each other in an unlimited way.
- * Part of the analytical data stored within the SOTER database might be questionable because in many cases it will be very difficult to find out with which method already introduced data were analyzed. As a consequence analytical data within SOTER have to be handled with care.
- * None of the four revised datasystems makes a statement regarding the most suitable or desirable analytical method for the determination of each of the physical and chemical attributes.

2.3 Chemical and physical attributes and their methods of analysis

The following attributes or soil properties as well as the different laboratory methods with which they can be determined were taken from the WISE database (Batjes, 1993). The list of attributes studied coincides almost completely with those selected by the IGBP-DIS working group members at Silsoe, October 1992. Each attribute is followed by a list of corresponding methods and a code. More methods might be included as the soil collecting programme for the WISE database proceeds. The list of methods is followed by some observations made by different authors from the Department of Soil Science and Plant Nutrition, Wageningen Agricultural University (author 1); the Department of Soil Science and Geology, Wageningen Agricultural University (author 2); the International Institute of Tropical Agriculture, Ibadan, Nigeria (author 3) and the

International Soil Reference and Information Centre (author 4). Personal comments of these authors are cited at random and indicated by "pc".

Organic carbon:

"OC--", "Not measured"

"OC01", "Method of Walkley/Black (Org. matter = Org. C x 1.72)"

"OC02", "Loss on ignition (NL)"

"OC03", "Method of Allison"

"OC04", "Method of Kurmies"

"OC05", "Method of furnace combustion (e.g. LECO)"

"OC06", "Method of Kalembra and Jenkinson (1973); acid dichromate; Org. matter = Org. C x 1.72)"

"OC07", "Wet oxidation according to Tinsley (1950)"

"OC08", "Method of Anne"

Author 1 (pc): method OC02, OC03 and OC05 determine total C, while method OC01 determines approximately 70-80% and OC04 99% of the total C.

Author 4 (pc): the results determined with each of the methods do not differ much and can be compared.

Total Nitrogen:

"TN--", "Not measured"

"TN01", "Method of Kjeldahl"

"TN02", "Hewlett Packard CHN 185 Analyzer"

Author 1 (pc): method of Kjeldahl (TN01) is a general name for a group of different analytical procedures to determine N and should be specified more in detail.

Phosphorus:

"TP--", "Not measured"

"TP01", "Total P; colorimetric in H₂SO₄-Se-Salicylic acid digest"

"TP02", "Method of Bray I (dilute HCl/NH₄F)"

"TP03", "Method of Olsen (0.5 M bicarbonate extraction)"

"TP04", "Method of Truog (dilute H₂SO₄)"

"TP05", "Method of Morgan (Na-acetate/acetic acid)"

"TP06", "Method of Saunders and Metelerkamp (anion-exch. resin)"

"TP07", "Method of Bray II (dilute HCl/NH₄F)"

"TP08", "Modified after ISFEI method, A.H. Hunter (1975)"

"TP09", "Method of Nelson (dilute HCl/H₂SO₄)"

"TP10", "ADAS method (NH₄ acetate/acetic acid)"

"TP11", "Na molybdate/hydrozinesulphate/dinitrophosphate"

Author 1 (pc): method TP01 is determining total P while all other methods TP02 to TP11 determine available P. For that reason the results of these two groups of methods can not be compared.

Each of the methods produces different results, especially because of its pH dependency. So P values of different soils determined by different methods can never be compared. The differences will be smaller when one soil type is analyzed by each of the methods.

- Author 3 (pc): the phosphorus content is pH dependent, determination by a lower pH will give a higher estimation of the available P. For that reason the P determined by Bray I < P determined by Bray II.
- Author 4 (pc): the about 70 existing methods are very different and give not comparable results. This is because of the complicated chemistry of phosphorus in the soil, at least as far as the assessment of P levels is concerned. The applicability of each of the methods is depending on soil conditions (mainly pH), while some of them measure the available phosphate and some the potentially available, also called fixed, phosphate. For instance Olson's method (TP03) is used for soils of pH > 7, whereas for acid soils the Bray (TP02 & 07), Truog (TP04) or Morgan (TP05) methods may be used (Landon, 1991).
- Etchevers (1986): the difference between available phosphate values depends on the pH of the extracting solutions and the shaking time. Bray-2 ((TP07) extracts more available P than Bray-1 (TP02) but less available P than Olson (TP03). The selection of the best extractant depends on soil type and the relationship between analytical values and the phosphorus absorbed by the growing plants.
- Kamprath (1986): studies with different groups of soils showed that Bray-1 (TP02) and Olson (TP03) extractable P gave the best correlation with labile P of calcareous and slightly weathered soils while Bray-2 (TP07) and Mehlich give the best estimates of labile P in highly weathered soils.
- Puh *et al.* (1971) TP02, TP03, TP04 and TP04 yield an inconsistent set of data for Thai land use systems and extraction data and field crop performance are poorly correlated.

Soil reaction (pH):

pH-H₂O

- "PH--", "Not measured"
- "PH01", "pH in 1:1 soil/water solution"
- "PH02", "pH in 1:2.5 soil/water solution"
- "PH03", "pH in 1:5 soil/water solution"
- "PH04", "pH in 1:2 soil/water solution"
- "PH05", "pH in water saturated extract"

pH-KCl

- "PK--", "Not measured"
- "PK01", "pH in 1:1 soil/1M KCl solution"
- "PK02", "pH in 1:2.5 soil/1M KCl solution"
- "PK03", "pH in 1:5 soil/1M KCl solution"
- "PK04", "pH in 1:2 soil 0.01 M KCl solution"

pH-CaCl₂

- "PC--", "Not measured"
- "PC01", "pH in 1:1 soil/1M CaCl₂ solution"
- "PC02", "pH in 1:2.5 soil/1M CaCl₂ solution"
- "PC03", "pH in 1:5 soil/1M CaCl₂ solution"
- "PC04", "pH in 1:2 soil/0.01 M CaCl₂ solution"

- Author 3 (pc): the differences between the measured values depend on the solid:liquid ratio: the pH in saturated extract < pH 1:1 suspension < pH 1:2 suspension < pH 1:2.5 suspension < pH 1:5 suspension.
- Author 4 (pc): the differences between pH values measured with 1: 2.5 and others measured with 1: 5 suspension ratios are small, as was found in The Netherlands. In the USA 1: 1 suspensions may give pH values which are consequently lower. The pH values from a saturated extract are normally only determined for saline soils, in addition to a "normal" pH determination in a soil suspension.

The following rules of thumb should be applied with great care: Dewis *et al.* (1970) indicate that pH values for 1:5 suspensions may generally be 0.5 to 1.5 units higher than values for corresponding saturated pastes. However the pH does not always rise, nor is any increase necessarily proportional to the dilution (Loveday *et al.*, 1972). For temperate soils, and many tropical ones, the use of 0.01M CaCl₂ suspensions is often favoured; values of pH in such suspensions are typically 0.5 to 0.9 units lower than in water, the difference usually being greater for neutral than for acidic soils. The use of KCl solutions may diminish the pH by one to two units compared with measurements in an equivalent aqueous suspension.

McIntosh (?): pH in 1:3 soil:water solution = 1.05 (pH field) + 0.55 (r = 0.77). However pH field values must be determined on a mixed bulk sample from the whole horizon and the moisture content of the sample must be adjusted in order to provide some standardisation between samples. It would be advisable to establish the relationship between field and laboratory measurements for batches of soils of different origins before using a universal adjustment factor or equation to predict "laboratory" pH.

Electrical Conductivity (EC):

"EL--", "Not measured"

"EL01", "Elec. conductivity in 1:1 soil/water solution"

"EL02", "Elec. conductivity in 1:2.5 soil/water solution"

"EL03", "Elec. conductivity in 1:5 soil/water solution"

"EL04", "Elec. conductivity in saturated paste (ECe)"

Author 4 (pc): The above mentioned conversion factors are dependent on the soil type, e.g. the clay % directly influences the ECe, and factors as mentioned by Landon (1991) must be handled with great care.

Landon (1991): When EC is measured on soil: water solutions that are more dilute than the saturation extract (and hence can be tested more easily since suction filtration is not required) the results cannot be interpreted directly from the salinity scale. There is no foolproof conversion factor that can be used to compare ECs at different soil: water ratios since even if the moisture characteristics of the soil are known, the solubility of the salts may vary with increasing dilution. However the following relationships (which are approximate and tentative) may be useful as a rough guide provided the samples do not contain significant amounts of gypsum:

ECe = 2.2 x EC1:1 (general experience)

ECe = 6.4 x EC1:5 (Talsma, 1968; Loveday *et al.*, 1972)

It is advisable to check the precise conversion factors between ECs at different soil: water ratios by obtaining the ECe from a representative number of samples and plotting these values against the EC dilution ratio.

Stace *et al.* (1976): 1:2.5 and 1:5 soil/water solutions are equally reliable for the determination of the electrolytic conductivity.

Total carbonate content:

"CA--", "Not measured"

"CA01", "Method of Scheibler (volumetric)"

"CA02", "Method of Wesemael"

"CA03", "Method of Piper"

"CA04", "Calcimeter method"

"CA05", "Gravimetric (USDA Agr. Hdbk 60; method Richards *et al.*, 1954)"

Author 4 (pc): The results determined with each of the methods do not differ much and can be compared.

Total gypsum content:

"GY--", "Not measured"
"GY01", "Acetone method"

Exchangeable bases (Ca⁺⁺, Mg⁺⁺, K⁺ and Na⁺):

"EX--", "Not measured"
"EX01", "Various methods with no apparent differences in results"

Author 3 (pc): a good agreement exist between exchangeable cations determined by method CS05 and by method CS01 and CS08.

Author 4 (pc): The results determined with each of the methods do not differ much and can be compared. For calcareous soils containing more than 2% CaCO₃ neither method CS01 nor method CS06 yield accurate figures for exchangeable Ca and BS due to the fact that both extractants dissolve greater or lesser amounts of Ca from the CaCO₃. Method CS08 or a solution of a neutral reacting salt is recommended (Grueneberg, 1986).

Landon (1991): Because of the strong effect of pH levels on clay content charge- and hence on ion adsorption- it is recommended that exchangeable cation measurements be made using an unbuffered saturating solution such as 1 M KCl at the pH of the soil (McLean, 1965). More widely accepted methods are:

- a) for soils without free carbonate: the ammonium acetate extraction at pH7.
- b) for soils with free carbonate: the sodium acetate method at pH 8.2.

Exchangeable acidity (Al⁺⁺⁺ and H⁺):

"EA--", "Not measured"
"EA01", "Exchangeable acidity in 1 M KCl"
"EA02", "Exch. acidity in 1 M KCl estimated from soluble Al in 2:1 v/v 0.02 M CaCl₂"
"EA03", "Extr. acidity in NH₄OAc, formaldehyde and BaCl₂; acid. by titration at pH 11 (Mados, 1943)"
"EA04", "Bariumacetate/ bariumhydroxide"

Cation Exchange Capacity (CEC):

"CS--", "Not measured"
"CS01", "CEC in 1M NH₄OAc buffered at pH 7"
"CS02", "CEC in 1M BaCl₂ buffered at pH 8.1"
"CS03", "CEC in 1M NH₄OAc buffered at pH 8.2"
"CS04", "CEC in 1M NaOAc buffered at pH 8.2"
"CS05", "CEC in unbuffered Silver Thiourea (AgTU)"
"CS06", "CEC as sum of bases (NH₄OAc at pH 7) plus acidity in BaCl₂-TEA buffered at pH 8.2"
"CS07", "CEC determined in 0.5 M LiCl buffered at pH 8 with TEA (after Peech, 1965)"
"CS08", "CEC in unbuffered 1 M KCl at pH of soil"

Author 3 (pc): A good agreement exist between exchangeable cations determined by method CS05 and by the methods CS01 and CS08 (Pleysier *et al.*, 1986). The CEC is directly pH dependent and a higher CEC value will be measured by making use of a more alkaline buffer solution. However for tropical soils, especially those which are acid and have a high OM content, the CEC determined at a pH of 7 or 8.2 will be estimated.

Determination of the unbuffered CEC (CS05 and CS08) will be in these cases more useful. CEC values determined with method CS05 and CS08 < CEC values determined with method CS01, CS02, CS03, CS04, and CS07 < CEC values determined with method CS06.

- Author 4 (pc): the existing methods are very different, soil dependent and give results which are not comparable. The result of a CEC measurement is very pH dependent because many soils have a variable charge (Grueneberg, 1986) and in general one can say that the CEC increases with pH.
Unbuffered extracts should be used as large deviations can occur when determinations are made at pH values far removed from the natural soil solution pH (Beech *et al.*, 1986). Determinations in unbuffered solutions are comparable (CS05 and CS08). Research done by ISRIC indicated that all measurements done at a pH of 7 are also comparable. Method CS06 will give much higher values because also extractable acidity is included.
- Beech *et al.* (1986): several methods of CEC determination are necessary to span a range of soil pH. It would be preferable if an extractant could be chosen which is suitable for all soil types. Until now agreement on such an extractant does not exist.
- Grueneberg (1986): investigations showed that the determination of CEC and exchangeable cations by method CS01 and CS06 will yield comparable results, provided the soils are not saline or calcareous. In the former case those soils that show a content of more than 1.0 meq soluble sulphate should not be determined using salts containing Ba as an extractant (methods CS02 and CS06), because precipitation of BaSO₄ will prevent correct determination of the adsorbed Ba. Method CS04 is recommended for these soils.
- Landon (1991): Standard methods for CEC determinations are given in Hesse (1971); for most projects the following methods are suitable:
- for variable-charge soils: 1 M KCl extraction at the unbuffered pH of the soil, but note that some exchangeable H and Al may not be measured.
 - for neutral soils which are not calcareous or saline: ammonium acetate extraction, adjusted to pH 7.
 - for other soils, notably saline and saline-sodic soils, and those containing Ca and Mg carbonates: sodium acetate extraction pH 8.2. The CECs in soils not having high sulphate contents can also be measured using 0.5 M BaCl₂/triethanolamine buffered to pH 8.2.

Effective Cation Exchange Capacity (ECEC):

"CE--","Not measured"

"CE01","Sum of exch. Ca, Mg, K and Na, plus exchangeable aluminium (in 1 N KCl)"

- Author 3 (pc): the ECEC by method CS05 correlates well with the ECEC for method CS01 and CS08. Deviations are mainly due to differences in extractability of Ca and Mg.

Base Saturation (BS):

"BS--","Not measured"

"BS01","Sum of bases as percentage of CEC (method specified above)"

- Kauffman (1987): BS of 35% (pH 8.2, "sum of cations")= BS of 50% (pH 7.0, NH₄OAc method CS01).
- Author 4 (pc): both in the determination of the sum of the bases as well as the determination of the CEC, errors can be made which can reinforce each other.

Particle size distribution/ Texture:

"TE--","Not measured"

"TE01","Pipette method, with appropriate dispersion treatment (c< 0.002 <si< 0.05 <sa< 2mm)"

"TE02","Pipette method, without dispersion treatment (c< 0.002 <si< 0.05 <sa< 2mm)"

"TE03","Hydrometer method, with dispersion treatment (c< 0.002 <si<0.05 <sa< 2mm)"

"TE04","Hydrometer, without dispersion treatment (c< 0.002 <si< 0.05 <sa< 2mm)"

"TE05","Pipette method, with appropriate dispersion treatment (c<0.002 <si< 0.02 <sa< 2mm)"

"TE06","Pipette method, without dispersion treatment (c<0.002 <si< 0.02 <sa< 2mm)"

"TE07","Hydrometer method, with dispersion treatment (c<0.002 <si< 0.02 <sa< 2mm)"

"TE08","Hydrometer, without dispersion treatment (c<0.002 <si< 0.02 <sa< 2mm)"

"TE09","Pipette method, with appropriate dispersion treatment (c< 0.002 <si< 0.06 <sa< 2mm)"

"TE10","Pipette method, without dispersion treatment (c< 0.002 <si< 0.06 <sa< 2mm)"

"TE11","Hydrometer method, with dispersion treatment (c< 0.002 <si< 0.06 <sa< 2mm)"

"TE12","Hydrometer, without dispersion treatment (c< 0.002 <si< 0.06 <sa< 2mm)"

Author 4 (pc): results are greatly affected by pretreatment and by the method itself, e.g. the shaking of the sample (Dewis and Freitas, 1970 in Landon, 1991). ISRIC by way of its LABEX programme found in the past that determinations by way of the pipette or the hydrometer do not show any significant difference (< 10%). The class limits, especially between silt and sand are very important, considering the fact that in the near future the limit will be 0.063. This limit is already used for civil-engineering analysis.

Houba *et al.* (1986): only in soils high in organic matter the fraction > 50 μm is higher in case no appropriate pretreatment (oxidation of M.O. by H_2O_2) is applied. For comparable data of the fractions < 50 μm it is necessary to sieve off the fraction > 50 μm first. Generally the hydrometer method gives somewhat higher results for the clay fraction (< 2 μm) and somewhat lower results for the silt fraction (< 20 μm).

Bulk density:

"BD--","Not measured"

"BD01","Core sampling (pF rings)"

"BD02","Clod samples"

"BD03","Replacement method (with spherical plastic balls; Avery & Bascomb, 1974)"

"BD04","Auger-hole method (Zwarich & Shaykewich, 1969)"

Author 4 (pc): The results determined with each of the methods do not differ much and can be compared. In general the determination of the bulk density is not too precise, and most sampling techniques introduce inaccuracy. Therefore density values have to be calculated until to one decimal.

Volume % of water at selected pF values:

"MC--","Not measured"

"MC01","sand/silt baths and porous plates, undisturbed samples (pF rings)"

"MC02","ceramic plate extractors, dist. samples in 10x50mm rings; after L.A. Richards 1965"

Author 4 (pc): The results determined with each of the methods do not differ much and can be compared.

Hydraulic conductivity:

"HC--", "Not measured"

"HC01", "Double ring method"

"HC02", "Bore hole method"

"HC03", "Inverse bore hole method"

2.4 Reliability of analytical results

Some laboratory data concern the composition and properties of soil material such as, for instance, the "soil reaction" (pH). Such data are often credited with being "hard" quantitative information but may not accurately reflect the properties of the natural soil if determined on material that was modified during pre-treatment of the sample (drying, grinding, sieving) or during the analysis procedure itself. Particularly if the material is analyzed under conditions that deviate strongly from those in the field (analysis in buffered solutions, high electrolyte concentrations, etc.), the data produced must be handled with care and may be inappropriate for use in for instance simulation studies (Driessen, 1986). Already in 1915 Robinson *et al.*, demonstrated the role of soil heterogeneity and emphasized the futility of improving analytical precision when field errors dominated.

Other laboratory tests have been developed to provide indexes of nutrient availability, such as the determination of available phosphorus or potassium. Generally, no one simple laboratory test will be applicable to all soils. Correlation studies should be conducted to provide the basis for selecting the laboratory test that will provide the best index of nutrient availability to plants in the soil samples to be tested. Correlations between plant test results and laboratory test results will serve as the basis for selecting the best laboratory test (Hanway, 1973). However excessive emphasis is often placed on the need for uniform laboratory procedures when the final product, i.e. the soil test results and recommendations, should also be an object of concern (Welch *et al.*, 1973).

Emphasis should be placed on the reliability of each of the analytical results before interpreting them or introducing new data into a database. As a first step a simple quality check of the data can be done. For instance, the CEC value of a soil must be directly related to the clay content and the organic matter content. If this is not the case the analytical results must be questioned and it is not recommendable to introduce indiscriminately the new data into a database (Van Reeuwijk, personal comment).

2.5 Universal applicability of laboratory methods and their standardization

Interpretations of laboratory results are seldom, if ever, universally applicable. Different methods may have to be employed on different soils to measure the same soil characteristic, and other influences (e.g. clay mineralogy, climate) will affect the interpretation of the same analysis on soils from different sites (Landon, 1991). Notwithstanding there is merit to minimizing the number of procedures used thus simplifying the process of comparing results, especially on similar soils obtained from different laboratories. Therefore a great deal of emphasis has been placed on the need for all soil testing laboratories to use the same procedures.

Recommendations as to the definitive choice of methods and details of procedures are difficult to make. Such a choice has not only purely technical but also historical implications. A laboratory, quite satisfied with the procedure which has been in use for many years, might not be readily prepared to adopt another method. The International Organization for Standardization (ISO) by way of its Technical Comity 190 working on "Soil Quality" is trying to achieve uniformity on analytical methods. Recommendations formulated by different Working Groups include the following elements and proposed methods (Houba, personal comment):

pH: in 1:5 soil/ water, KCl or CaCl₂ solution on volume/volume basis

CaCO₃: volumetric

CEC: in 1M BaCl₂ buffered at pH8.2

ECEC: in 0.01M BaCl₂ unbuffered

EC: in 1:5 soil/ water ratio on weight/volume basis

On the short term agreement can be expected on the following elements and methods:

- N (avail.): extraction by 0.01M CaCl₂
C: method of furnace combustion
wet oxidation with K₂Cr₂O₇-H₂SO₄
P: method of Olson (0.5M bicarbonate extraction)

Further testing and correlation of methods by more laboratories seems to be another option (Van Reeuwijk, 1982 & 1983). A helpful step in this direction is the exchange of standard samples. Such samples are available to laboratories for the purpose of relating their results to those reported by other laboratories. This offers a laboratory the opportunity to check their techniques and compare results. How the results are obtained is less important than how well they correlate with each other and with crop response.

All reports of interlaboratory comparison schemes emphasize the importance of cross-checking, and the feasibility of standardization seems to be indicated. Despite this, however, even after thorough standardization, a certain minimum level variation will appear to be unavoidable. From the ISRIC exchange programme LABEX the following estimates of attainable variability of some important parameters were made (Van Reeuwijk, 1982): Clay content: 11%; CEC of the clay: 25%; Base saturation: 10%. Certain disturbing factors such as sampling variability, seasonal variation and contaminations have even not been taken into account.

The wide variation in the results reported within the LABEX program indicate that even when the methods are standardized, no absolute agreement between the results from different laboratories is achieved. The skill and experience of the laboratory assistants, as well as the conditions in the laboratory, i.g. the climatic conditions, the type and state of the laboratory equipment, the quality of the water amongst other factors may be of greater importance than standardization of methods used (Grüneberg, 1986). This is clearly illustrated by some investigations carried out in Argentina which showed that no success was achieved in reducing the considerable variations for the analysis of nitrogen (Morras, 1986).

2.6 Conclusions and recommendations

- * The key question is if the method for determining the total content of a certain element does or does not influence the final result.
- * Different analytical methods have their origin in different technical (e.g. degree of accuracy) and historical causes. Therefore the results of determinations carried out on the same soil type can differ considerably.
- * A comparison of results obtained with different methods shows that direct relations expressed in a mathematical way (regression equations) occasionally exist. If they are found they take into consideration a limited amount of methods and are only valid for a specific soil type.
- * It is not realistic to expect that on the short term global agreement will be achieved on the most reliable and desirable analytical method for each soil attribute in order to obtain full standardization. This should make it easier to compare and to interchange all data stored within different databases in an unambiguous way.
- * Experiences show that even when analytical methods are standardized a certain minimum level of variation will appear to be unavoidable. For some pedologists this variation, at least for some soil attributes, will be acceptable.
- * For the purpose of discussion it might be useful to subdivide laboratory methods into two main groups (Van Mensvoort, personal comment):
 - a) analysis focused on the general characterisation of the soil.
 - b) analysis which can provide indexes of nutrient availability.Examples of the first group are pH, Organic Carbon and EC. Examples of the second group are Available Phosphorus, Nitrogen and Potassium.

The impression exists that the results from the first group of laboratory methods are easier to compare than the results from the second group. The reason for this is that attributes obtained by analytical methods of the first group can usually be defined quite clearly, and rather satisfactory methods are available to get an impression of the potential qualities of a soil. Lack of true understanding of the processes governing the availability of nutrients has led to the development of an ever-increasing

number of methods falling into the second group, each claiming preference for use under specified conditions (Houba *et al.*, 1988).

- * Only one method was specified for the determination of Total Nitrogen and Total Gypsum, so interchange of data between databases might be possible.
- * Determination of Available Phosphorus, CEC, Texture and Hydraulic Conductivity is carried out by complex procedures of which principles can vary considerably. For these attributes it is therefore recommendable to accept a large variability in results for granted.

3 CATION EXCHANGE CAPACITY (CEC)

3.1 Introduction

The cation exchange capacity (CEC) of a horizon or sample is the total number of exchangeable cations it can retain on its adsorbent complex at a given pH (Baize, 1993). The CEC is a reversible reaction in the soil solution and may arise from permanently charged or pH-dependent sites on organic and mineral colloid surfaces (Soil Survey Laboratory Staff, 1992). CEC measurements are commonly a part of the overall assessment of the potential fertility of a soil, and possible response to fertiliser application (Landon, 1991).

3.2 Methods to determine CEC

It is well known that the CEC is not a soil property that is independent of the conditions under which it is measured. Different results will be obtained with different methods. They all are based on the same principle (Baize, 1993):

- * displacement of the exchangeable cation(s) and H^+ by a solution containing a single ion of similar electrical charge or sign (NH_4^+ , Ba^{2+} , H^+ , Li^+ , $AgTU^+$).
- * saturation of the sample with the cation of this solution.
- * displacement of the adsorbed "replacement ion" by a second "replacement ion" and then determination of the first one.

Factors which affect results include size of the replacement ion, the affinity for particular ions and exchange sites, the associated anion, ionic strength, the soil and solution pH, soil/solution ratio, and time of contact between soil and solution (Rayment *et al.*, 1992). The presence of soluble salts of the basic cations like halite (NaCl), gypsum ($CaSO_4 \cdot 2H_2O$), lime ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) can also cause errors in estimation of exchangeable bases.

Ideally the method to determine CEC is one that measures the soil's capacity to adsorb cations from an aqueous solution of the same pH, ionic strength and composition as that encountered in the field, since CEC varies (especially in tropical soils) with these parameters. This is however very impractical and in addition, it is desirable that the analytical results of each of the methods can be compared and interchanged. For these reasons CEC determinations are generally done using standardized conditions (Rhoades, 1982).

The following methods, for the greater part taken from the WISE database, can be a.o. distinguished:

- * CEC as sum of bases (NH_4OAc at pH 7) plus extractable acidity in $BaCl_2$ -TEA buffered at pH 8.2"
- * CEC in 1M NH_4OAc buffered at pH 7"
- * CEC in 1M $NaOAc$ buffered at pH 8.2"
- * CEC in 1M $BaCl_2$ buffered at pH 8.2"
- * ECEC as sum of bases plus Al (exchangeable acidity in 1 N KCl)
- * CEC in 1M NH_4OAc buffered at pH 8.2"
- * CEC in unbuffered Silver Thiourea ($AgTU$)"
- * CEC determined in 0.5 M LiCl buffered at pH 8 with TEA (after Peech, 1965)"
- * CEC in unbuffered 1 M KCl at pH of soil"
- * CEC in unbuffered 1 M NH_4Cl at pH of soil"
- * CEC in 1 M NH_4Cl buffered at pH 8.5"

Because of the strong influence of the method on the results, the method of determination of CEC should always be reported. CEC is not an absolute constant for a particular soil but may have a range of values according to the cation involved in its determination (Dewis *et al.*, 1970).

3.3 Comparison of methods

Unfortunately CEC values are markedly dependant on the method chosen for their determination (Gillman *et al.*, 1983). Most methods for the determination of CEC rely on saturation and displacement at high solution concentrations. However, Moller *et al.* (1953) found that addition of chemicals affect the colloid structure of the soil and Larsen (1964) maintained that the extractant changes the chemistry of the soil to such an extent that it is doubtful whether such results have any bearing on the soil in its natural state.

Although numerous methods have been developed for measuring exchangeable cations in soils, they generally use one or the other of two types of extractants: buffered or unbuffered salts (Amacher *et al.*, 1990). Comparisons of CEC methods have shown that buffered salt methods give higher CEC values than do unbuffered salt methods, if the soils being measured have a pH-dependent charge. The negative charge increases significantly with the pH and ionic strength of the solution, and as a result the number of the sites capable of retaining cations increases (Guadalix *et al.*, 1988). An over-estimation of the ability of variable charge soils to retain cations in the field is therefore likely to occur (Gillman *et al.*, 1983).

Houba *et al.* (1990) compared BaCl_2 (method 4 ?) with AgTU (method 7) in unbuffered conditions. Soil samples without carbonates show almost the same CEC value. When carbonates are present (higher pH- H_2O values) the CEC values determined using AgTU are somewhat higher compared to the values found using unbuffered BaCl_2 . Arbelo *et al.* (1991) observed that for some volcanic soil samples the AgTU values are also similar to BaCl_2 values. They also compared the BaCl_2 -TEA (pH 8.2) (method 1 ?) and NH_4OAc (pH 7) (method 2) methods in buffered conditions. When the pH of the buffered solution, used for the determination of the CEC, deviated much from the real pH of the soil sample, the resulting values of the CEC differ substantially, yielding a higher CEC value for the BaCl_2 -TEA method than for the NH_4OAc method. Grueneberg (1986) stated that the small differences between the results of the two methods may be neglected, provided the CEC does not exceed 25 me/100 g soil and no soluble sulphates are present (precipitation of BaSO_4).

Hanna *et al.* (1948) found CEC values for limed soils determined by buffered BaCl_2 (method 4) which were considerably higher than those for the NH_4OAc method (method 2). Most of the variation in CEC between the two procedures could be explained on the basis of differences in amounts of exchangeable hydrogen measured by the two procedures. The same result was obtained some years later by Pratt *et al.* (1954) and by Peech *et al.* (1962).

Conradie *et al.* (1989) observed that CEC values obtained by the sum of the exchange acidity and extractable cations were considerably higher than those by the NaOAc method (method 3). Measuring of CEC in unbuffered AgTU (method 7) gave the lowest CEC values. Guadalix *et al.* (1988) observed the contrary for some Andosols with variable charge. The NaOAc method gave much higher values than the effective CEC determination, as well as the BaCl_2 method (method 4). This effect was greater when the variable charge was higher as a result of soil mineralogy and organic matter content.

The CEC values for some calcareous soils from Egypt as determined by NaOAc (method 3) are considerably higher than those determined by NH_4OAc (method 2). Amer (1960) explains this difference by emphasizing the variation in the pH of solutions used for saturating the soil, the former was adjusted to pH 8.2 and the latter to pH 7. This argument was later questioned by Peech *et al.* (1962).

According to Pleysier *et al.* (1980) and Beech *et al.* (1986) results of the AgTU method (method 7) generally agree with those of the NH_4OAc (method 2) method for exchangeable cations and CEC.

For some soils, considerable differences in extracted cations between the methods occur. Chhabra *et al.* (1975) found large differences between CEC by unbuffered AgTU and by neutral NH_4OAc for acid soils with high organic matter content. Also Arbelo *et al.* (1991) found for some volcanic soil samples very high CEC values determined with NH_4OAc in comparison with values obtained by the AgTU method. Gillman *et al.* (1983) demonstrated the need for caution in predicting soil behaviour from CEC determined at a pH higher (NH_4OAc method) than soil pH (AgTU method): in some of the variable charge soils studied they observed that "field" CEC values were only 1/3 of the NH_4OAc values.

The NH_4OAc method (method 2) gives slightly higher results than the NH_4Cl method (method 10) (Kalra *et al.*, 1991); differences can be significantly higher for soils with a high pH-dependent CEC. The study of Gillman *et al.* (1983) who compared the NH_4OAc method with a buffered NH_4Cl solution (method 11), revealed that reasonable agreement between the methods was obtained for constant charge soils. Variable charge soils however, showed higher CEC values for sub-surface samples, which were obtained by means of the NH_4OAc method. Surface samples of these variable-charge soils showed the opposite, the values of the NH_4Cl method were higher.

The NH_4OAc exchangeable cations plus BaCl_2 -TEA exchangeable acidity procedure (method 1) yielded higher CEC values for the Ultisols studied by Horn *et al.* (1982) than the CEC obtained by the buffered NH_4OAc method (method 2) and the ECEC values determined with the NH_4OAc exchangeable cations plus KCl exchangeable Al method (method 5).

3.4 Prediction of CEC values using data regression

It is interesting to develop a method of prediction, that is, a procedure for estimating the CEC value of a certain method from experimental information from another one. The statistical aspect of the problem then becomes one of arriving at the best estimate of the relationship between the results of the two different CEC methods. The relationship, fitted to a set of these results, is characterized by a prediction equation called a regression equation (Walpole *et al.*, 1978).

In order to derive a mathematical expression that relates one method to another it was necessary to find a set of data presenting more than one CEC value for identical soil samples, each of them determined by a different method. Such a set of data is presented by the U.S. Soil Conservation Service (1975), which used seven analytical methods to determine the CEC of soils in the U.S.A.. Also Fenger *et al.* (1986) present CEC data from tropical soils of Tanzania determined by two different methods (method 2b and 3). The following methods were employed by U.S. Soil Conservation Service (1972) and Fenger *et al.* (1986) to analyze the soils:

1. CEC as sum of bases (NH_4OAc at pH7) plus acidity (5A3)
extractable acidity by BaCl_2 -TEA at pH 8.2 (5A3a)
2. CEC in 1M NH_4OAc buffered at pH7 (5A1)
 - a. direct distillation of adsorbed ammonia, Kjeldahl (5A1a)
 - b. displacement and distillation of adsorbed ammonia, semimicro Kjeldahl (5A1b)
 - c. direct distillation making use of leaching tubes (5A6a)
3. CEC in 1M NaOAc buffered at pH8.2 (5A2)
centrifuge method (5A2a)
4. CEC in 1M BaCl_2 at pH8.2 (5A5)
Ba by flame photometry (5A5a)
5. Effective Cation Exchange Capacity (ECEC)
sum of bases plus Al (exchangeable acidity) (5A3b)

Each method used in the laboratory is also indicated by a code number (put in brackets) which corresponds to the numeration as used by Soil Conservation Service (1972). Method 2a, 2b and 2c differ from an analytical technical point of view but the nature of the CEC determination does not vary.

3.5 Comparison of selected data

Of the 130 pedons presented in Soil Taxonomy, 57 pedons were selected for which the CEC was determined by means of at least two different methods. The pedons were located in different parts of the United States and belong to the following soil orders:

Alfisols	(12 pedons)
Aridisols	(1 pedon)
Entisols	(1 pedon)
Inceptisols	(5 pedons)
Mollisols	(16 pedons)
Oxisols	(5 pedons)
Spodosols	(4 pedons)
Ultisols	(10 pedons)
Vertisols	(3 pedons)

Fenger *et al.* (1986) present 53 pedons belonging to four different soil orders, of which for 25 pedons the CEC was determined by means of two different methods:

Alfisols	(9 pedons)
Inceptisols	(1 pedon)
Mollisols	(4 pedons)
Vertisols	(11 pedons)

It is clear that the number of pedons belonging to each soil order differs greatly between one and another and as a consequence also the number of CEC values used to compare one method with another. This last number is indicated in Table 1 by the code "n". Table 1 presents also the different regression equations which relate one CEC method to another, each of them indicated by the same codes as have been presented in section 3.4.

Data regression can compute the coefficient values and constant for a formula that ties one or more ranges of independent variables (x) to a range of dependant variables (y). With that the regression equation can be formed that relates one CEC method to another and which can serve to predict a value for a dependant variable based on the values for one or more independent variables.

The CEC of some soil orders has only been determined by two methods while for other orders various methods have been used. The latter can be perceived from Table 1 when for the same soil order more then one column is filled in.

3.6 Limitations with respect to data regression

The results for linear regression depend on the assumption that the true relationship between x and y is linear. This can be checked by determining the r^2 values which calculate the percentage of the total variability in the data which is explained by the regression line. For a simple regression between two variables it is the square of the correlation coefficient between the two variables x and y (Mead *et al.*, 1993). Estimates of the coefficient of determination (r^2) close to unity in magnitude imply a good linear association between x and y , while values near zero indicate the absence of such an association.

For Inceptisols, for instance, the r^2 value relating method 1 to method 2 is 0.96 (Table 3.1.) which means that 96% of the variation in the values of y (determined by method 2) is accounted for by a linear relationship with x (determined by method 1). Since r^2 is 0.53 for Mollisols, one can say that only 53% of the variation in the values of y (determined by method 5) is accounted for by a linear relationship with x (determined by method 3). Therefore it is questionable if there exist any linear association.

Aside from merely estimating the linear relationship between the results of one CEC method and the results from another for prediction purposes, it is useful to know something more about the general quality of the

estimated regression line. This in order to prevent that regression results are presented without any reference to how well the regression line will predict response. This can lead to misinterpretations and even improper use of the information.

A useful instrument to prevent this is the determination of the prediction interval on a future observed response. A 95% prediction band on the whole regression line is widely used and a figure can display the data points, the estimated regression line and the upper and lower confidence limits. As an example the regression results of CEC data for Inceptisols and Mollisols (Table 3.1.) are presented in a graphic way (Fig. 1 and 2).

Figure 1 shows clearly that the regression equation for Inceptisols can predict the response rather well. Most measured CEC values, indicated within the figure by "+", are located inside the 95% prediction band. For Mollisols (Figure 2) half of the measured CEC values are located outside the prediction band which means that the regression equation is not predicting very well the response and consequently must be handled with great care.

3.7 Conclusions and recommendations

- * positive and negative charges of tropical soils are mainly pH dependent while the negative charges of the soils of temperate regions are mostly permanent. The CEC of soils of the temperate regions, in which the CEC is largely dominated by the permanent negative charge, can be analyzed satisfactorily by salt solutions at some specified pH value, often 7 or 8 (Van Raij *et al.*, 1972).
- * as opposed to clays or soils with constant charge, the cation exchange capacity (CEC) of many tropical soils with variable charge depends to a large extent on the method used for determining it. The methods for determining the CEC differ widely regarding the use of buffered or not buffered solutions, the pH of the buffer solution, ionic strength of the displacing solution and the valence of the saturating and displacing cation and anions (Gangaiya *et al.*, 1987). Therefore the character of the required extraction solution and the operation necessary to dissolve an element or the compound that contains it affect the results, which makes the compatibility of CEC data very difficult.
- * saline, calcareous, alkaline and alkali soils need special techniques for the determination of exchangeable cations and CEC.
- * although for some soil orders the number of CEC values taken from Soil Taxonomy used for carrying out a data regression is very small it appears that the found regression equations well express the linear relationships between the independent variable x (CEC values found by method 1) and the dependant variable y (CEC values found by method 2a) which is expressed in the high values for r^2 . An exception are Vertisols for which the r^2 value is rather low ($r^2 = 0.64$). As a consequence the regression equation for Vertisols is not very reliable.
- * methods 2a, 2b and 2c can be considered as variations on one and the same method. When each of them is compared with method 1 it appears that the r^2 values are low. Comparing the combined results with those of method 1 gives as a result some regression equations which express well the linear relationship between one and another.
- * method 4 and 5 are only used to determine a small number of CEC values for Ultisols. There exist two well fitting regression equations expressing the linear relationship between the results of each of these methods and those obtained by method 1.
- * for Aridisols and Vertisols there exist a well fitting regression equation expressing the linear relationship between the results of method 2a and those obtained by method 3. However the number of CEC values is small.
- * moderately high r^2 values are found for Alfisols and Vertisols when CEC values of soils from Tanzania are compared, determined with method 2b and method 3, respectively. For Inceptisols and Mollisols the r^2 values are too low to find a well fitting regression equation and a linear relationship between method 2b and method 3 does not exist for these soil orders.
- * it will be useful to determine the influence of pH and organic carbon content as independent variables on the CEC values generating more complex relations than the linear ones studied until now.
- * it is recommended to repeat the exercise of deducting relationships between CEC values obtained by different methods, from soils of other climatic regions.

Table 1. Regression equations for CEC values presented by Soil Conservation Service (1975) and Fenger *et al.* (1986) corresponding to different soil orders comparing two methods. Values of the first method are handled as independent variables (x), values of the second method as dependant variables (y) which can be predicted in the future (r^2 = coefficient of determination; n = number of CEC values used; $s.e.(x)$ = standard error of x-coefficient; $s.e.(y)$ = standard error of y estimation).

compared methods (x,y) ▶	1,2a	1,2b	1,2c	1,2	1,3	1,4	1,5	2a,3	2b,3	
Soil Order ▼	Soil Conservation Service								Fenger <i>et al.</i>	
Alfisols	$y=0.79x+0.07$ $r^2= 0.94$ $n= 67$ $s.e.(x)=0.02$ $s.e.(y)=1.54$	$y=0.89x-3.67$ $r^2= 0.85$ $n= 5$ $s.e.(x)=0.22$ $s.e.(y)=2.21$		$y=0.78x+0.10$ $r^2= 0.94$ $n= 72$ $s.e.(x)=0.02$ $s.e.(y)=1.59$	$y=0.96x+1.31$ $r^2= 0.93$ $n= 14$ $s.e.(x)=0.08$ $s.e.(y)=1.32$					$y=1.32x+8.96$ $r^2= 0.85$ $n= 45$ $s.e.(x)=0.08$ $s.e.(y)=4.93$
Aridisols								$y=1.05x+0.89$ $r^2= 0.99$ $n= 9$ $s.e.(x)=0.04$ $s.e.(y)=0.69$		
Entisols	$y=0.39x+0.90$ $r^2= 0.92$ $n= 5$ $s.e.(x)=0.07$ $s.e.(y)=0.14$									
Inceptisols	$y=0.75x-0.38$ $r^2= 0.99$ $n= 12$ $s.e.(x)=0.03$ $s.e.(y)=1.45$		$y=0.78x-2.00$ $r^2= 0.95$ $n= 9$ $s.e.(x)=0.07$ $s.e.(y)=6.17$	$y=0.77x-1.11$ $r^2= 0.96$ $n= 21$ $s.e.(x)=0.03$ $s.e.(y)=3.91$					$y=3.19x-18.5$ $r^2= 0.49$ $n= 5$ $s.e.(x)=1.87$ $s.e.(y)=4.25$	
Mollisols	$y=0.75x+0.99$ $r^2= 0.96$ $n= 99$ $s.e.(x)=0.02$ $s.e.(y)=1.73$								$y=0.91x+20.5$ $r^2= 0.53$ $n= 26$ $s.e.(x)=0.18$ $s.e.(y)=5.57$	
Oxisols	$y=0.66x-1.51$ $r^2= 0.86$ $n= 33$ $s.e.(x)=0.05$ $s.e.(y)=2.02$									
Spodosols	$y=0.41x+0.15$ $r^2= 0.97$ $n= 8$ $s.e.(x)=0.03$ $s.e.(y)=0.68$		$y=0.97x-9.20$ $r^2= 0.89$ $n= 19$ $s.e.(x)=0.08$ $s.e.(y)=15.15$	$y=0.94x-5.98$ $r^2= 0.92$ $n= 27$ $s.e.(x)=0.06$ $s.e.(y)=12.91$						
Ultisols	$y=0.69x+0.60$ $r^2= 0.92$ $n= 42$ $s.e.(x)=0.03$ $s.e.(y)=1.53$		$y=1.38x-13.51$ $r^2= 0.75$ $n= 3$ $s.e.(x)=0.81$ $s.e.(y)=1.03$	$y=0.69x+0.60$ $r^2= 0.92$ $n= 45$ $s.e.(x)=0.03$ $s.e.(y)=1.49$		$y=0.91x-0.08$ $r^2= 0.99$ $n= 24$ $s.e.(x)=0.02$ $s.e.(y)=0.48$	$y=0.28x-0.11$ $r^2= 0.71$ $n= 8$ $s.e.(x)=0.07$ $s.e.(y)=0.51$			
Vertisols	$y=0.67x+3.59$ $r^2= 0.64$ $n= 14$ $s.e.(x)=0.15$ $s.e.(y)=1.79$							$y=1.20x-3.47$ $r^2= 0.96$ $n= 7$ $s.e.(x)=0.11$ $s.e.(y)=0.60$	$y=1.28x+9.88$ $r^2= 0.85$ $n= 62$ $s.e.(x)=0.07$ $s.e.(y)=5.66$	

INCEPTISOLS

CEC in 1M NH₄OAc buffered at pH7

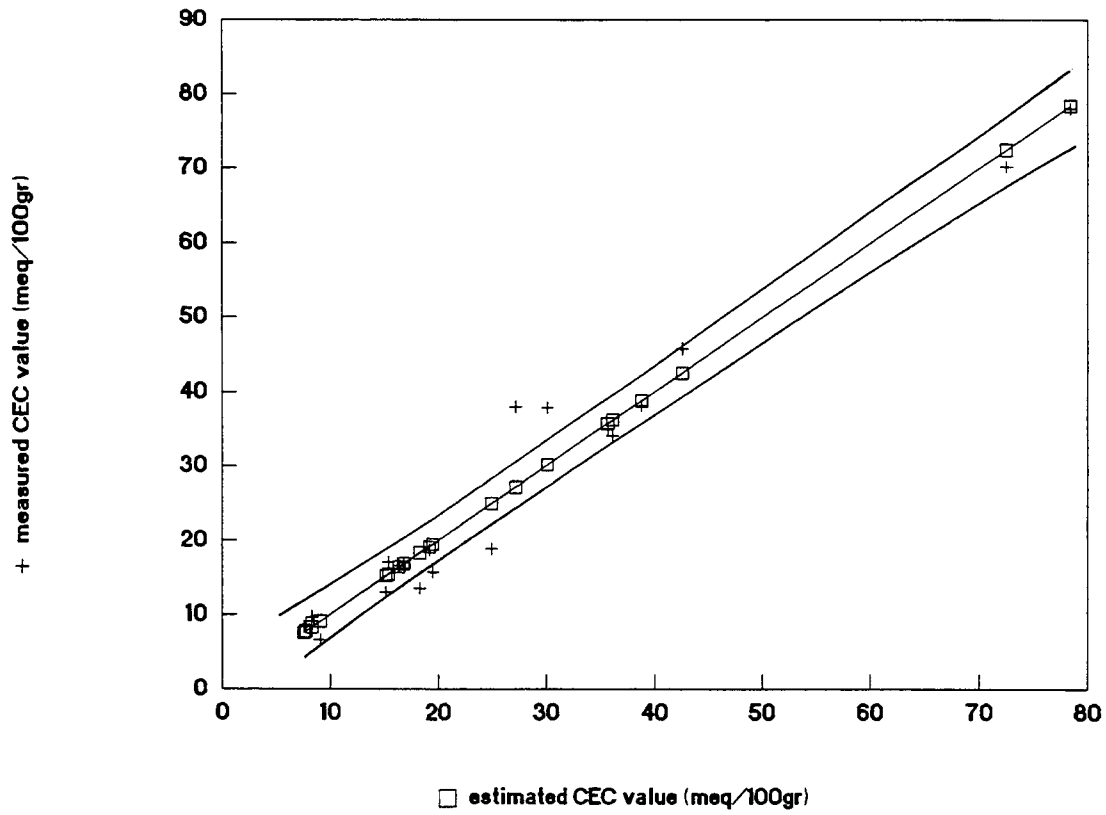


Figure 1. CEC data points, the estimated regression line and the upper and lower 95% confidence limits for Inceptisols.

MOLLISOLS

CEC in 1M NaOAc buffered at pH8.2

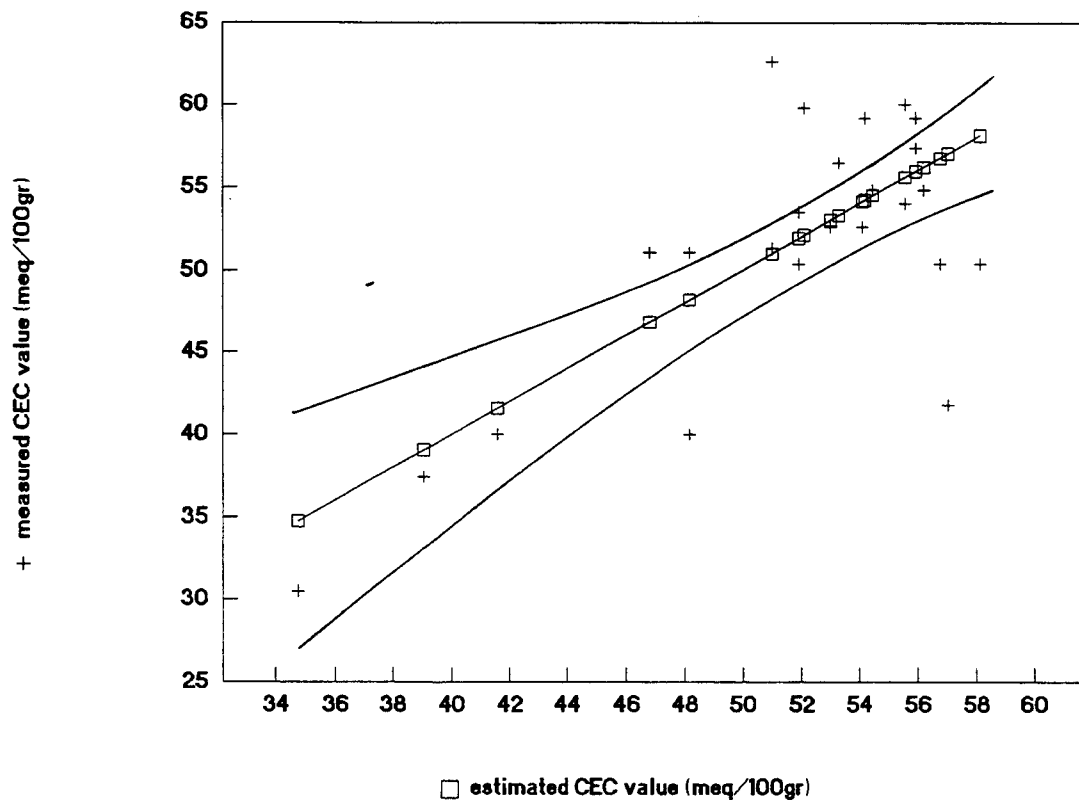


Figure 2. CEC data points, the estimated regression line and the upper and lower 95% confidence limits for Mollisols.

4 ORGANIC CARBON

4.1 Introduction

Total carbon in soils is the sum of both organic and inorganic carbon. Most organic C is present in the soil organic matter fraction, whereas inorganic C is largely found in carbonate minerals. Not all soils contain inorganic C because of dissolution during soil formation of carbonate minerals originally present in parent material. However, organic C is present in all agricultural soils (Nelson and Sommers, 1982).

4.2 Methods to determine organic carbon

Methods for the determination of organic carbon all have in common the oxidation of the organic C to CO₂. The oxidation can occur by dry combustion or by wet combustion. The C is determined by a direct measurement of the formed CO₂, or by an indirect measurement, e.g. weight loss of the sample, or excess of the added oxidant. The following table of Begheyn (1986) presents some current methodologies for the determination of organic C in soils.

1. Dry combustion

1.1 Indirect method

1.1.1 Loss on ignition (LOI)

Temperature: 850 °C; detection by weight loss, representing the mass of soil organic matter burnt to CO₂ and lost; recovery 100% (after possible correction); no corrections are made for losses in weight caused by the decomposition of certain carbonates (e.g. dolomite), volatilization of e.g. sulphides and dehydration of hydrated iron oxides. This implies that the method is recommended for well aerated samples with low contents of clay minerals; that is sandy and peat soils only (Houba *et al.*, 1988).

1.2 Direct methods

1.2.1 LECO (Tabatabai and Bremner, 1970)

Temperature: 1400-1600 °C; detection of CO₂ by thermal conductivity (IR).

1.2.2 USDA (Soil Investigation Report no 1)

Temperature: 1000 °C; detection of CO₂ by gravimetry (after absorption); recovery 100%.

2. Wet combustion

2.1 Indirect methods

2.1.1 Use of K₂Cr₂O₇ + H₂SO₄

2.1.1.1 Walkley-Black

Heat source: spontaneous heat of dilution generated by mixing H₂SO₄ with K₂Cr₂O₇ solution causing oxidation of organic matter by Cr₂O₇²⁻; detection: titration with Fe⁺⁺ of excess K₂Cr₂O₇; recovery: 70- 84%.

2.1.1.2 Kermies

Heat source: boiling waterbath; detection: titration with KMnO₄ of excess Fe⁺⁺ over K₂Cr₂O₇, or by means of spectrophotometric determination; recovery: 98%.

2.1.1.3 Schollenberger

Heat source: external, 175 °C; detection Cr⁺⁺⁺ (colori- or titrimetric); recovery: 86.9%.

2.1.1.4 Anne

recovery: ± 93%

2.1.1.5 Mebius

recovery: 92- 110%

2.1.1.6 Tinsley

recovery: 88- 106%

2.1.2 Use of $\text{KMnO}_4 + \text{H}_2\text{SO}_4$

2.1.2.1 Ischtscherekow

Heat source: boiling waterbath; detection: oxidation of excess KMnO_4 with oxalic acid, titration of excess ox.acid with KMnO_4 ; recovery: unknown.

2.2 Direct methods

2.2.1 Use of $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ (3:2)

2.2.1.1 Allison

Heat source: external, 210 °C; detection of CO_2 by gravimetry (in absorbent); recovery: 100%.

Indirect wet combustion methods (method 2.1) are universally used and the Walkley-Black method (1934) is perhaps the best known. In principle the method consists of adding an oxidizing agent (dichromate) to a sample and back titrating the excess agent. It is assumed that oxygen reacts only with organic matter however Driessen (1992) indicates some mayor limitations:

- * The results are influenced significantly by the (reaction) temperature during the oxidation of the samples. Excessive heat can cause the decomposition of the $\text{K}_2\text{Cr}_2\text{O}_7$ added or lack of heat can mean that oxidation of the organic material is incomplete (Etchevers, 1986).
- * The colour transformation of the indicator used for the titration is often neither sharp nor clear (partly by interference of the soil colour) resulting in a high dependence on the personnel judgement of the final result.
- * Actually not the C% is determined but the amount of oxygen consumed by the soil components. Thus samples containing easy oxidizable compounds such as Fe^{2+} (FeS_2 in sulfidic soils) and Mn^{2+} , which occur in reduced soils, will yield too high C% data. This also means that low C data imply low amounts of pyrite, what is useful in tracing potential acid sulphate soils.
- * Certain forms of carbon such as charcoal and coke in regions of human habitation, and undecomposed plant residues do not react with the oxidizing agent, resulting in too low figures (Landon, 1991). The question remains however if these forms of C are of interest in these determinations.

4.3 Comparison of methods

Bremner *et al.* (1960), Tabatabai *et al.* (1970), Kalembasa *et al.* (1973) and Nelson *et al.* (1975) found that a very good agreement is obtained when direct wet combustion (2.2), dry combustion (1.1 & 1.2) and Van Slyke-Folch (1940) methods are used to determine organic C in soils. For this reason these methods are normally considered to yield absolute values for organic C in soils. Other methods such as indirect wet combustion methods (2.1.1) that involve a period of heating like, for instance Anne (1945), Mebius (1960) and Tinsley (1950) or that make use of the spontaneous heat of dilution like Walkley-Black, are calibrated against them.

Bremner *et al.* (1960) found that the Tinsley method gave organic C-values for 15 soils that varied from 88 to 106% (avg 101%) of direct wet combustion values. Kalembasa *et al.* (1973) showed that the Tinsley method yielded organic C recoveries from 22 soils that varied from 92 to 103% (avg 95%) of direct wet combustion values. Nelson *et al.* (1975) observed that the Mebius method (method 2.1.1.5) recovered from 92 to 110% (avg 103%) of the organic C found in 10 soils by the direct wet combustion procedure. Frattini *et al.* (1967) found a high correlation coefficients ($r^2= 0.96$) between dry combustion and the Schollenberg method (method 2.1.1.3). Soon *et al.* (1991) compared three indirect wet combustion methods (Tinsley, Mebius, and Walkley-Black method) with a loss-on-ignition method (method 1.1.1) and the dry combustion procedure (method 1.2.1) for the determination of organic C in soils from Canada. Results indicate that Tinsley and Mebius recovered 95% and 98%, respectively of soil C, as compared with the dry combustion method. The loss-on-ignition method was generally unreliable for soils of lower organic C (<15 mg C/g) content, although precision can be improved if clay content is also considered as a variable. All procedures gave correlation coefficients of 0.98 or better against the dry combustion method.

Many studies have shown that the Walkley-Black method provides variable recovery of organic C from soils, because in some soils >90% of the organic C may be oxidized, whereas with other soils <70% of organic C

is converted to CO₂. This rate of oxidation is dependent on the nature of soil organic matter (Van Moort *et al.*, 1970). Because of this uncertainty it is assumed very often that the Walkley-Black method oxidizes 75% of the carbon, and therefore a correction factor of 1.33 (the inverse of the fraction oxidized) is used to convert the C-value determined to the total C (Allison, 1965). This arbitrary factor is widely used, although Grewal *et al.* (1991) suggested an average conversion factor of 1.25 and Soon *et al.* (1991) of 1.4. Taking into account the position in surface or subsurface horizon the individual conversion factors can even vary between 1.1 and 1.6, corresponding to 85% to 62% of recovery, respectively. Sanchez *et al.* (1973) previously reported, that the percent recovery decreases with depth. Contrary to these findings, Bornemisza *et al.* (1979) observed for some Andept profiles that organic C in deeper horizons is easier to oxidize and, as a result, the conversion factor should be smaller.

Edwards and Todd-Ross (1983) used correction factors for "high temperature dry combustion/ Walkley-Black" of 1.08, 0.90 and 1.38 for the 0-15, 15-30 and 30-45 cm depth zones, respectively. Richter *et al.* (1990) used the 'uncorrected' Walkley-Black value because according to these researchers the correction factors vary too widely.

The above figures clearly indicate that indirect wet combustion methods such as the Walkley-Black method that involve minimal heating give variable recovery of organic C from soils. An average correction factor found for a group of soils may be applicable to the "average" soil in the group but will give erroneous values for many soils in the group. Therefore, procedures such as the given by Walkley-Black should be considered to give approximate or semiquantitative estimates of organic C in soil because of the lack of an appropriate correction factor for each soil analyzed (Nelson and Sommers, 1982).

4.4 Expression of soil organic matter content

Assuming that the soil organic matter contains 50% carbon, the factor 2 is used to convert the total organic carbon to total organic matter (humus). It is clear that this value may vary considerably. Values varying between 30% and 63% carbon in organic matter can be expected mainly depending on source of origin and age of the organic material (degree of humification) (Houba *et al.*, 1990). Nelson and Sommers (1982) determined a range of 0.40 to 0.59 for the C/OM ratio depending upon soil type and soil depth. Baize (1993) suggests a factor 1.7 which seems better suited for ploughed horizons, while 2.0 is more appropriate for forest topsoils. As a consequence of the uncertainty about an appropriate ratio Baize (1993) and also Nelson and Sommers (1982) recommend to work with the figures for carbon rather than those for organic matter, which are estimated approximately.

4.5 Conclusions

- * Carbon values determined by means of the dry combustion method (methods 1.1 & 1.2) as well as the direct wet combustion method (method 2.2.1.2) are comparable because they are able to recover 100% of the organic C.
- * Indirect wet combustion methods (methods 2.1) like Kurmies, Tinsley and Mebius are able to recover most of the organic C and the results of these methods are comparable with results obtained by dry combustion or direct wet combustion. The original Walkley-Black method however provides a variable recovery of organic C from soils and the correction or recovery factor used to convert the C-value determined to the total C, varies greatly from one soil to another. Results obtained by this method give therefore an approximation of organic C in soils and they are difficult to compare with results from other methods.

5 SOIL REACTION (pH)

5.1 Introduction

A potentiometrically determined soil pH is essentially an index of hydrogen ion (H^+) activity in solution at equilibrium with soil particles (Van Lierop, 1990). The soil reaction is measured and presented as the pH value, which is defined as the negative logarithm of the H-ion concentration (ranging from 10^{-1} to 10^{-12} mol/l). The higher the H-ion concentration, the lower its negative logarithm, or pH value, and the more acid the soil reaction.

The soil pH is affected by many factors, e.g. temperature, nature and type of inorganic and organic constituents that contribute to acidity, amount and type of exchangeable cations and anions, soil:solution ratio of the soil suspension, salt or electrolyte content of the soil suspension, CO_2 pressure, and specifications of the equipment used. The acidity, neutrality, or alkalinity of a soil influences the solubility of various compounds, the relative bonding of ions to exchange sites, and the activities of various microorganisms (McLean, 1982; Soil Survey Lab. Staff, 1992).

5.2 Methods to determine soil reaction

Schofield *et al.* (1955), White (1969) and Rusell (1973) have suggested that the main criteria for selecting an extractant for pH measurement is that it should cause a minimum of disturbance to the distribution of ions between soil surfaces and the soil solution. An extractant that has the same ionic strength as the soil solution and is made up of the most common ions present in the soil may provide the most realistic pH measurement. However such an approach would be very time consuming, as the ionic strength of each soil would have to be determined before pH measurement. A compromise would have to be achieved by using an ionic strength that represented the average value in a certain group of soils.

Routine soil pH measurements are usually made on extracts from soil suspensions, which vary from saturated soil pastes to soil suspensions at a ratio of 1:5 soil/liquid. After settling, soil pH is measured in the supernatant fluid with glass-calomel electrodes. The dilution medium normally consists of water. The presence of salts generally (highly sesquioxenic soils excepted) results in a decrease in the soil pH, since soluble salts can repel H^+ ions from the exchange complex and displace aluminium which will hydrolyze. This can be overcome by using diluted solutions of $CaCl_2$, instead of water which is thought to condition the salt effect without displacing much H^+ and Al^{3+} from the exchange complex. The contrary is taking place with making use of KCl which expels all or nearly all H^+ and Al^{3+} ions from the exchange complex. As a consequence the concentrations of the test solutions are more representative of the salt concentrations in natural soil solutions. The pH values obtained are consequently less dependant on the soil dilution ratio and are therefore more reproducible (Schofield *et al.*, 1955).

The presence of active aluminium in soils is assessed by measuring the soil reaction with a NaF solution (Van Reeuwijk, 1993). When immersed in a solution of NaF, active Al adsorbs F^- ions with a consequent release of OH^- ions, leading to higher pH values. The pH-NaF may be used as an indicator that amorphous material dominates the soil exchange complex (Soil Survey Laboratory Staff, 1992).

Taking into account the above mentioned dilution media it is possible to divide the methods to determine soil reaction into four main groups. Subdivision can take place according to the dilution ratio.

1. pH- H_2O

- 1.1 pH in 1:1 soil/water solution
- 1.2 pH in 1:2.5 soil/water solution
- 1.3 pH in 1:5 soil/water solution
- 1.4 pH in 1:2 soil/water solution
- 1.5 pH in saturated extract (for saline soils)

2. pH-KCl

- 2.1 pH in 1:1 soil/1M KCl solution
- 2.2 pH in 1:2.5 soil/1M KCl solution
- 2.3 pH in 1:5 soil/1M KCl solution
- 2.4 pH in 1:2 soil 0.01 M KCl solution

3. pH-CaCl₂

- 3.1 pH in 1:1 soil/1M CaCl₂ solution
- 3.2 pH in 1:2.5 soil/1M CaCl₂ solution
- 3.3 pH in 1:5 soil/1M CaCl₂ solution
- 3.4 pH in 1:2 soil/0.01 M CaCl₂ solution"

4. pH-NaF

- 4.1 pH in 1:50 soil/1M NaF solution

5.3 Comparison between methods

Dilution ratio has been extensively discussed in literature (Peech, 1965; Foth *et al.*, 1988; Soil Survey Laboratory Staff, 1992), and most sources indicate that pH values in water increase with the dilution of the suspension. With other words: if conditions are the same, the more water added to a soil sample, the higher the pH (or the more the H ions are diluted). Of course, for most soils, conditions are not identical; hence the dilutions of H⁺ by addition of water is partially compensated for by additional dissociation of H⁺ (McLean, 1977).

Coleman *et al.* (1967) states that differences of several tenths of a pH unit are observed in going from 1:10 to a 1:1 soil:liquid mixture. Stace *et al.* (1968) in their compilation on Australian soils indicate that values for pH as determined in 1:1 and 1:5 soil/water solution (method 1.1 and 1.3) and 1:2.5 soil/CaCl₂ solution (method 3.2), in some soils, range over almost 2 pH units. However in 1976 the same author finds that 1:2.5 and 1:5 soil/water solutions (method 1.2 and 1.3) are equally reliable for the determination of the pH (Stace *et al.*, 1976). Also Krupskiĭ *et al.* (1969), Schachtschabel (1971) and ILACO (1981) state that the values of pH measured in a 1:2.5 soil/water solution (method 1.2) deviate slightly from those obtained by making use of a dilution ratio of 1:1 and 1:5 (method 1.1 and 1.3).

Houba *et al.* (1990) studied for 14 Dutch soil types the influence of soil-solution ratio and the position of electrodes (solution or suspension) on measurements of pH-H₂O and pH-KCl. They found that the ratio used is of very small influence on the pH values measured and that they are independent of electrode position. The latter was not found by Yoshida *et al.* (1974) who reported small differences between pH values determined in aqueous suspensions or, after settling, in the supernatant. When soils were suspended in 1M KCl solutions, such differences due to suspended particles were not observed.

The pH values of a saturated paste (method 1.5) are always lower than the values measured in a 1:2.5 soil/water solution (method 1.2), because of less dilution and higher H-ion concentrations. Mubarak *et al.* (1976) showed that below 1:1 ratios, the pH is dependent on moisture content. Dewis *et al.* (1970) is even more precise and indicates that pH values for 1:5 suspensions may generally be 0.5 to 1.5 units higher than values for corresponding saturated pastes. However the pH is not always higher, nor is any increase necessarily proportional to the dilution (Loveday *et al.*, 1972).

For temperate soils, and many tropical ones, the use of 0.01M CaCl₂ suspensions is often favoured (method 3.4); values of pH in such CaCl₂ suspensions are typically 0.5 to 0.9 units lower than in water, the difference usually being greater for neutral than for acidic soils (Schachtschabel, 1971; Dolling *et al.*, 1985; Conyers

et al., 1988; Landon, 1991). Smaller differences are possible when soils contain high levels of soluble salts and/or when soil colloids exhibit variable surface charge (Rayment *et al.*, 1992). Davies (1971), Rytí (1965) and Kalra *et al.* (1991) indicate a mean difference of 0.5 pH units for mineral soils and Stanek (1973) of 0.6 pH units for a paste of freshly peat rewetted with 0.01M CaCl₂ in comparison to peat rewetted with water. Van Lierop *et al.* (1977) found average pH values for organic soils which were 0.55 pH units lower. Some years later the difference was found even smaller, 0.44 pH units (Van Lierop, 1981). Converting data by merely adding or subtracting the average difference between methods appeared however not to be as accurate as using appropriate regression equations. Little (1992) found a non-linear relationship due to the buffering effect of Al at low pH and to the presence of carbonate at high pH.

Measuring pH in a KCl suspension is particularly applicable to acidic, highly weathered soils dominated by colloids with variable surface charge characteristics. Except for certain strongly weathered tropical soils with a high anion exchange capacity, the use of KCl solutions may reduce the pH by one to two units compared with measurements in an equivalent aqueous suspension (Baize, 1993; Houba *et al.*, 1990; ILACO, 1981; Soil Survey Lab. Staff, 1992). Van Lierop *et al.* (1977) and Van Lierop (1981) indicate a more exact difference of 0.7 pH units for organic soils and Starek (1973) of 0.5 units for a paste of freshly peat rewetted with 0.1M KCl.

Foth *et al.* (1988) stated in general that when salt solutions of CaCl₂ or KCl, in the range of 0.07 to 1M are used, soil pH values may be 0.5 to 1.5 units lower than when they are measured with distilled water.

Houba *et al.* (1990) found a clear relationship between pH-KCl and pH-CaCl₂ values for non-calcareous soils. Both values appeared to be almost equal, which is confirmed by the findings of Schachtschabel (1971) and Van Lierop (1981) and by Feige (1973) for organic soils. Soil pH values measured with KCl or CaCl₂ suspensions, were practically independent of the soil-solution ratios used (Duch, 1963; Van Lierop, 1981; Davey *et al.*, 1988, Kalra *et al.*, 1991).

5.4 Conclusions

- * pH values measured in water increase in some cases with the dilution of the suspension. The increase is however not proportional and is sometimes not observed.
- * The pH values of a saturated paste are always lower than the values measured in a soil/water solution, because of less dilution and higher H-ion concentrations.
- * For temperate soils, and many tropical ones 0.01M CaCl₂ suspensions are often used. Measuring pH in a KCl suspension is particularly applicable to acidic, highly weathered soils dominated by colloids with variable surface charge characteristics. The soil pH of both mineral as organic soils, determined by using water is normally 0.5 to 1.5 units higher than pH values measured in diluted solutions of CaCl₂ and KCl, respectively.
- * pH values for non calcareous soils, measured in CaCl₂ or KCl are almost equal and independent of the soil-solution ratios used.
- * Converting data by merely adding or subtracting the average difference between methods appeared not to be as accurate as using appropriate regression equations. Occasionally a (non)-linear relation between the results of different methods (pH-H₂O, pH-KCl and pH-CaCl₂) is found as well as between different suspension ratios and their corresponding pH values.

6 BULK DENSITY

6.1 Introduction

Bulk density refers to the overall density of a soil, i.e. the mass of mineral soil, determined after drying to constant weight at 105 °C, divided by the overall volume occupied by the solid, liquid and gas phase. It is ordinarily expressed in units of g/cm^{-3} . The term bulk density is preferred to the terms volume weight, bulk specific gravity or apparent specific gravity (Blake, 1965). Bulk density should not be confused with the density of only the solid soil constituents, usually called the particle density or specific gravity, which excludes pore spaces between particles (Landon, 1991; Head, 1980).

Bulk density is a widely used soil attribute. It is needed for converting water percentage by weight to content by volume, required for computing the available water capacity. When the particle density is known, bulk density can also be used to calculate the soil porosity. And bulk density is a prerequisite for estimating the weight of a volume of soil too large to weigh conveniently, such as the weight of the arable layer.

Bulk density is not an invariable parameter for a given soil. It varies with the structural condition of the soil, particularly that related to packing. Also the volume of soil may vary as water content changes. So bulk density is actually a function rather than a single value. Therefore some laboratories add subscripts to the bulk density notation, D_b , to designate the water state of the sample when the volume was measured (Soil Survey Lab. Staff, 1992).

6.2 Methods to determine bulk density

The methods available for the measurement of bulk density fall into two groups: direct and indirect methods. In the first group are the long-established methods, which require removing and weighing the soil from a known or measured volume. They differ principally in the way the sample of the soil is obtained:

1. Replacement methods

1.1 Replacement with spherical plastic balls.

A hole of about 20 cm x 20 cm area x 10 cm deep is carefully cut at the desired depth. The removed soil is dried and weighed. The original volume occupied by the soil is then determined by recording the number of spherical plastic balls of known packing density that are required to fill the hole. The method is accurate and applicable on most soils. However it is slow, since minimum disturbance of the soil surrounding the hole is required.

1.2 Replacement with sand.

Instead of plastic balls (method 1.1), sand is used to fill the hole.

It is used on all soil types, also on sloping terrain. However the method is slow (test time about 30 minutes), and in fissured soils the sand tends to run into the cracks, resulting in an over-estimate of soil volume. The sand should be closely graded to prevent segregation (Campbell *et al.*, 1991) and has to remain perfectly dry.

1.3 Replacement with a water-filled rubber balloon.

Instead of plastic balls (method 1.1) a rubber balloon is inserted into the excavated hole and it is filled with a volume of water which is measured. Unreliable results are associated with entrapped air and with the dependence of the fit of the balloon in the hole on the air pressure (Campbell *et al.*, 1991).

1.4 Replacement with water lining the hole with a plastic film.

A bench must be cut into soils on sloping terrain so that a level surface exists. Proper sampling becomes difficult for shallow surface horizons on sloping terrain (Flint *et al.*, 1984).

2. Core method

Taking an undisturbed core sample of soil using a coring cylinder (often referred to as a pF ring) of known volume, which is pressed or driven into the soil and then carefully dug out to preserve a known volume of a sample as it existed in situ. The larger the volume of the cylinder, the better. Replicate sampling is however recommendable. In wet soils soil friction on the sides of the core causes viscous flow and thus compression. In dry soils the sample may shatter. The method cannot cope with sandy, gravelly or stony soils. However, an undisturbed soil sample, horizontally or vertically taken, is considered appropriate for non-destructive physical tests.

3. Auger-hole method

Using a 10 cm diameter auger, a hole 15 cm deep is bored, and the oven-dry weight of the extracted soil is determined. The volume of the hole is calculated from the measurements of depth and cross-sectional area. It is more accurate than method 2 but a uniform hole has to be made and the removed soil is completely disturbed.

4. Clod method

4.1 Water displacement.

A clod is weighed and its volume is determined by coating it with paraffin wax to prevent absorption by water, and immersing it in a volumometer. The volume of water displaced corresponds to that of the clod plus wax. Alternatively, the waxed clod may be weighed in air and water. Instead of dipping the clod into paraffin wax also a rubber solution or SARIN resin can be used. The method gives satisfactory results, however it is limited to cohesive soils and it is rather slow. It will yield relatively high bulk density values because the measurement can exclude the natural pore space between clods and between clods and rock fragments (Flint *et al.*, 1984; Buol *et al.*, 1989).

4.2 Kerosene displacement.

Like method 4.1, however kerosene is used instead of water.

4.3 Mercury displacement.

Like method 4.1, however the clod is not coated and mercury is used instead of water.

4.4 Weighing in water.

A clod is weighed in air and its volume is determined by coating it in paraffin wax and immersing it for weighing in water, making use of Archimedes' principle (Head, 1980).

Some general observations can be made regarding to the implementation of the direct methods:

- * Bulk density values vary considerably with moisture content, particularly those of fine-textured soils which can swell or shrink; samples should therefore be taken at or near to field capacity (Landon, 1991).
- * All methods of bulk density measurement may be hindered by the presence of stones, mainly because they can cause sample disturbance (Vomocil, 1957; Campbell *et al.*, 1991).
- * Bulk density replicates at a site may vary considerably; variations of at least 15 to 20 percent are to be expected in most soils (Landon, 1991). Therefore at least three replicate determinations are normally made at each side, but for detailed work up to 10 may be required. Even in horizons of similar texture lying at similar depths, there are usually great differences in bulk density values depending on organic matter levels, root penetration and soil structure.

The second group of indirect methods have been developed in which the transmission or scattering of nuclear radiation by soil are used to estimate the density of the combined liquid-solid components of a soil mass. Correction by determining the water content of the soil at sampling time is necessary to remove the component of density attributable to liquid that is present (Blake, 1965). Both radiation methods are in situ methods.

In the transmission technique, two probes at a fixed spacing are lowered into previously prepared openings in the soil. One probe contains a Geiger tube, which detects the radiation transmitted through the soil from

the gamma source located in the other probe. The scattering technique employs a single probe containing both gamma source and detector separated by shielding in the probe. It can be used either at the soil surface or placed in a hole, depending on the design of the equipment.

These radiation methods are more accurate, precise, and faster in operation, and measurements can be made at close intervals down a soil profile with little disturbance and/or can be repeated in time (Baize, 1993). However, high costs and requirement for compliance with radiation safety regulations are two major drawbacks. The transmission technique is more accurate than the scattering method.

The indirect methods are less used by both agricultural soil scientists and civil engineers and will be therefore used in this paper only as a reference to evaluate the accuracy of the different direct methods.

6.3 Comparison of methods

Some comparisons have been made of the various direct methods available. Core sampling (method 2) and the clod method (method 4) give similar results, while the sand replacement (method 1.2) values are about 2% lower (Anon., 1964; Yoro *et al.*, 1990). Tisdall (1951) however found the contrary: the sand replacement method (method 1.2) yielded higher density values ($\pm 3\%$), which were even exceeded by auger hole values (method 3). Also the difference between values for clod and core samples was greater ($\pm 2\%$). Zwarich *et al.* (1969) also concluded that the sand replacement method yield higher values than the core method and values obtained by the former method were similar to those obtained by the auger-hole method.

Cunningham *et al.* (1968) evaluated soils with a high amount of coarse fragments and found that in spite of the sampling problems, core sampling (method 2) was the most suitable for determining bulk density. Density values are lower (about 10%) than those obtained by the replacement method (method 1.4) or the replacement method with a water-filled rubber balloon (method 1.3) (Andraski, 1991). Clod samples (method 4.1) yield slightly higher density values than those determined by core sampling and can be collected in soils containing many coarse fragments. Also Burgos *et al.* (1967) concluded this, while McIntyre *et al.* (1968) observed the same, making use however of kerosene displacement (method 4.2).

It looks like an exception that Palta *et al.* (1969) found larger differences between different methods. They observed that the water displacement by a clod coated with paraffin wax (method 4.1) gives apparently lower density values (about 20%) than those obtained by the core sampling (method 2) and the sand replacement method (method 1.2). Density values of clods determined by displacement of kerosene (method 4.2) and mercury (method 4.3) were even higher (about 5%) and almost comparable.

The difficulty in extracting soil samples from the field without disturbance to the sample and to the wall of the remaining hole means that none of the direct methods of measuring bulk density can be relied on to be totally accurate. For most soils the core sampling method is generally taken to be the standard method. This in spite of its many inherent errors and its uselessness in situations where looseness of the soil prevents its retention within the core. In that case the sand replacement method is the best option.

Several comparisons between direct and indirect gamma-ray measurements have found general agreement between the two methods. King *et al.* (1959) as well as Mintzer (1961) obtained data which indicated a reasonable agreement ($\pm 3\%$) between a single-probe gamma gauge and the sand replacement method (method 1.2) in sandy and clayey soils but unacceptable large differences of 11% in gravelly soils. Ward *et al.* (1993) concluded that soil core bulk density values were highly correlated to the gamma gauge results (r^2 of 0.92 for wet bulk density). Gameda *et al.* (1983) compared single- and twin-probe gauges with the core-sampling method (method 2) on three soils to a depth of 0.6 m. A good correlation was found between both methods for sandy and clayey soils but not for loamy soil. Soane *et al.* (1970) found that on three contrasting mineral soils, density measurements from a twin-probe gamma gauge agreed with corresponding core sample measurements (method 2) within 3% but that there was a discrepancy of about 25% on low density organic peat samples. Baize (1993) states, however, that bulk density values measured on clods (method 4) are not absolutely comparable to those determined by radiation methods as loose aggregates are not constrained by their neighbours.

6.4 Conclusions

- * For most soils the core sampling method is generally taken to be the standard method, although the method is somewhat unsatisfactory for stony or noncoherent samples.
- * Bulk density values determined by the core sampling method are comparable with values obtained by the clod method, which measures displacement of water.
- * Other less common methods like the sand replacement method, the auger-hole method and the clod method which measures displacement of mercury or kerosene instead of water, yield in most cases bulk density values which deviate only a few percent from the values obtained by the core method.
- * Indirect methods making use of the scattering or transmission of nuclear radiation by soil yield density values which do not differ much from values determined by different direct methods. However, soils with an very specific composition, like gravelly soils or peaty soils yield unacceptable large differences.

7 VOLUME PERCENT OF WATER AT SELECTED pF VALUES

7.1 Introduction

All free moisture contained in the pore space of a soil is subject to capillary forces. This capillary pull causes a negative soil moisture tension, or positive suction, which is expressed as the height of the water column that would rise from the water table, against the force of gravity. This height is inversely proportional to the diameter of the pores. The term matric potential is often used synonymously except that its sign is opposite. It results from the attractive forces between the soil matrix and the water.

Particle size distribution, clay mineralogy, organic matter (due to its hydrophilic nature) and soil structure determine the specific relationship between the pF values (decimal logarithm of the matric potential in cm water head) of a certain soil and the corresponding moisture contents by volume (Kalra *et al.*, 1991; Soil Survey Lab. Staff, 1992). The relationship can be plotted as a curve, called the pF curve, also referred to as the soil moisture characteristic (curve), soil water retention function, and soil water release characteristic (ILACO, 1981; Klute, 1986).

The curve is determined by bringing a soil into equilibrium with various moisture tensions and then measuring its moisture content by weight. The curve is useful for the following purposes:

- * to indicate the ability of a soil to store water that will be available to growing plants
- * to indicate the aeration status of a drained soil
- * to be interpreted in non-swelling soils as a measure of pore size distribution

7.2 Methods to determine water retention values

Diverse methodologies for the determination of water retention values for pF curves have been developed. The most important techniques and the ranges of suction for which each method can be used are presented by Reeve *et al.* (1991):

1. Buchner funnel	0- 20 kPa*
2. Porous suction plate	0- 70 kPa
3. Sand suction table	0- 10 kPa
4. Sand-kaolin suction table	10- 50 kPa
5. Porous pressure plate	0- 1500 kPa
6. Pressure membrane	10- 10,000 kPa
7. Centrifuge	10- 3000 kPa
8. Osmosis	30- 2500 kPa
9. Consolidation	1- 1000 kPa
10. Vapour pressure (vacuum desiccator)	3000- 1,000,000 kPa
11. Sorption balance	3000- 1,000,000 kPa
12. Filter paper	1000- 10,000,000 kPa

Note: (*) 100 kPa \approx 1 bar \approx 10³ cm water head \approx pF3

The methods are based upon two distinct procedures to obtain a pF curve. The usual way is to equilibrate samples at a chosen range of potentials and then to determine their moisture contents. Suction tables (method 3 and 4), pressure plates (method 5 and 6) and vacuum desiccators (method 10) are the best-known examples of this approach. In the second approach, samples are allowed to dry out progressively and their potential and moisture content are both directly measured.

The samples for determining the retention curve may be either repacked samples or samples of natural structure. Since the structure of the sample affects the water retention, especially in the lower suction range (pF 0- pF 2.7), it is generally best to use undisturbed samples with natural structure. For the high suction range (pF 3.4 and pF 4.2) disturbed samples are normally used (Van Reeuwijk, 1993).

"Field Capacity" (pF 2 or 2.5 are both used= 9.8 and 31 kPa respectively) and "Permanent Wilting Point" (pF 4.2= 1568.6 kPa) are two arbitrary points on the pF curve necessary to calculate the available moisture in a soil. This is defined as the volume of water retained between both values and as such a useful agricultural concept.

Field methods of determining the pF curve are done in situ and consequently are more representative than laboratory measurements. By installing tensiometers at different depths in the field, suction readings of potential can be related to water content measurements determined either gravimetrically or by a neutron probe. However, if the soil rewets between readings, hysteresis can be a problem, and fluctuations in the soil temperature cause further complications through their effect on the viscosity of soil water. For these reasons, field methods are less commonly used than laboratory methods and will be left out of consideration in this paper.

7.3 Comparison of methods

Errors arising from the execution of laboratory procedures are likely to exceed the differences resulting from the use of alternative methods. Any attempt at standardization should start with sampling procedure and sample preparation. These are major factors in analytical differences, and a correct choice of sample state and sample size will largely decide the analytical technique used (Reeve *et al.*, 1991).

Few data are published which compare the different methods to determine water retention values. Waters (1980) found for 17 mineral and 3 peat soils that ceramic/porous pressure plate extractors (method 5) provide moisture contents comparable to those from pressure membrane apparatus (method 6) at the same applied pressure of 15 bar (permanent wilting point). However the former method is preferred to the latter for reliability and ease of determining.

Salter *et al.* (1965) and also Ratliff *et al.* (1983) compared field measured limits of soil water availability as related to laboratory measured properties. They found that if absolute accuracy is necessary in water balance calculations, laboratory estimated soil water limits should be used with caution. Field-measured limits are usually a more attractive alternative if they are available. Also Chahal *et al.* (1965) showed that the soil moisture characteristic curve determined with the pressure membrane may not represent the actual condition of soil water as encountered by the growing plant.

7.4 Conclusions

- * Few references can be found in the literature which compare different methods to determine water retention values. The reason for this is that each method is used for a different range of suctions, in order to bring a soil into equilibrium with a defined tension followed by the determination of the moisture content by weight.
- * Field methods are done in situ and results are consequently more reliable than those from laboratory measurements.

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Annex 1 Review of analytical information which forms part of the ISIS, FAO-ISRIC SDB, SOTER and WISE database.

ISRIC Soil Information System - ISIS (Van Waveren *et al.*, 1988)

- * Physical analysis
- * Chemical analysis
- * Elemental composition clay
- * Elemental composition soil
- * Soluble salts
- * Clay mineralogy
- * Sand mineralogy
- * Additional analysis: used to enter variables that are not included in the previous screens and to add remarks on the analytical data.

FAO-ISRIC Soil Data Base

- * Standard analyses: up to 12 user defined analyses
- * Determination on saturated paste (soluble salts): methods
- * Soil physical data (infiltration, water retention): methods

Coded information on the methods used should be entered under the heading 'Methods'. Up to 10 entries (one code each) can be combined in this field. Use always the same position(s) for the same variable. For your convenience the positions in the field are numbered from 0 to 9.

SOil and TERrain digital database - SOTER (Van Engelen *et al.*, 1993)

Laboratory information: for every analysis method that has been applied in a particular laboratory separate entries in these tables should be made.

Laboratory:

- * Lab-ID: identification code for the laboratory that analyzed the reference soil profile. A country code with a sequential number is given.
- * Laboratory name: name of the laboratory, in full (up to 40 characters).

Laboratory method:

- * Lab-ID: laboratory code (see above)
- * Date: date at which the laboratory introduced a method for a given attribute. Format is MM/YYYY.
- * Attribute: profile layer attribute that was analyzed.
- * Method of analysis-ID: identification code for the analysis method applied. This code consists of the attribute code followed by a sequential number.

Analytical method:

- * Method of analysis: method code
- * Description: a complete description of the analytical method used. There is room for 256 characters.

World Inventory on Soil Emissions - WISE (Batjes, 1993)

- * Chemical data
- * Physical data

Measured data are to be entered for both the chemical and physical attributes, indicating the methods of analysis and the laboratory where the analysis have been carried out. Coding conventions for the different analytical methods used to determine a specific attribute have been developed and will be amplified as the international data collection programme proceeds.

A concise summary, as a text string of at most 50 characters, of the analytical method (e.g. organic carbon according to Walkley and Black method) can also be included within the laboratory methods file (description part).