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Viktória Vona

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SZÉCHENYI ISTVÁN UNIVERSITY
FACULTY OF AGRICULTURAL AND FOOD SCIENCES
DEPARTMENT OF WATER AND ENVIRONMENTAL SCIENCES AND
DEPARTMENT OF BIOSYSTEMS AND FOOD ENGINEERING

Wittmann Antal Multidisciplinary Doctoral School
of Plant, Animal, and Food Sciences

Head of Doctoral School:

Prof. Dr. László Varga DSc
Full Professor

Haberlandt Gottlieb Plant Science Doctoral Program

Program Chair:

Prof. Dr. Vince Ördög DSc
Full Professor

Dissertation Supervisors:

Dr. habil. Renátó Kalocsai PhD
Associate Professor, Head of Department

Dr. habil. Attila Kovács PhD
Associate Professor, Head of Department, Deputy Dean of International Relations

Comparison of Phosphorus, Magnesium and Zinc Determination Methods on Hungarian Soils

Written by:

VIKTÓRIA VONA

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Írta:

Viktória Vona

Készült a Széchenyi István Egyetem Mezőgazdaság- és Élelmiszer-tudományi Kar Wittmann Antal Növény-, Állat- és Élelmiszer- tudományi Multidiszciplináris Doktori Iskola
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Témavezetők: Dr. Habil. Kalocsai Renátó, Dr. Habil. Kovács Attila

Elfogadásra javaslom (igen / nem)

(aláírás)

A jelölt a doktori szigorlaton………..%-ot ért el,

Mosonmagyaróvár, ………………………………

……………………………….
a Szigorlati Bizottság Elnöke

Az értekezést bírálóként elfogadásra javaslom (igen/nem)

Első bíráló (Dr. ……………………………..……) igen/nem

(aláírás)

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(aláírás)

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(aláírás)

A jelölt az értekezés nyilvános vitáján ………..%-ot ért el.

Mosonmagyaróvár, ………………………………

A Bírálóbizottság elnöke

Doktori (PhD) oklevél minősítése……………….……

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Abstract

This thesis aims to summarize the Hungarian soil analysis methods that have a background from decades of work and compare them with other internationally used methods. Our current soil testing system still provides usable results today, but following international trends, the domestic adoption of newer soil testing methods may provide new perspectives in the methodology of Hungarian soil testing. There are several methods used worldwide and each country has its own validated methods, best-suited for its soils. The harmonization of methods, measurements and indicators for the sustainable management and protection of soil resources is increasingly important to comply with the tightening legislation and boundary conditions for sustainable agricultural production. In the harmonization process, it is important to understand the background of our existing methods to work out a methodology that helps to compare and interpret the results of the different methods.

The current study was designed to compare the Hungarian soil analysis methods AL (ammonium lactate), KCl (potassium chloride), KCl-EDTA (potassium chloride ethylenediaminetetraacetic acid) methods with Mehlich 3, water extraction, CoHex (cobalt hexamine) and XRF (X-ray fluorescence) methods. The different nutrient analysis methods were compared for phosphorus, magnesium and zinc measurements with 70 samples from Hungary.

Data were first compared for the whole dataset and then, in certain categories of calcium carbonate content, pH, liquid limit according to Arany and clay content. Based on these results, it can be concluded that not only the well-known extraction methods and the soil but also the chosen classification method of the soil properties and also, the statistical analyses (measuring all data or certain classes) affect the evaluation of phosphorus, magnesium and zinc measurements. This comparative analysis study can provide a guide to compare and interpret the different analyses methods towards harmonization.

Foszfor, magnézium és cink módszerek összehasonlító vizsgálata magyarországi talajokon

Kivonat

A dolgozat célja az volt, hogy áttekintsük a több évtizedes múltra tekintő magyarországi talajvizsgálati módszereinket és összehasonlítsuk ezeket más nemzetközileg alkalmazott módszerekkel. Jelenlegi talajvizsgálati rendszerünk jól felhasználható eredményeket szolgáltat ma is, azonban a nemzetközi trendeket is követve, az újabb talajvizsgálati módszerek hazai adaptálása új perspektívákat nyújthat a hazai talajvizsgálatok, tápanyag-gazdálkodás módszertanában. Világszerte többféle talajvizsgálati módszert alkalmaznak, és minden országnak megvannak a saját talajaikra validált módszerei. A talaj, mint erőforrás fenntartható kezelésével és védelmével kapcsolatos módszerek, mérések és indikátorok összehangolása egyre fontosabb annak érdekében, hogy megfeleljünk a szigorodó jogszabályoknak és a fenntartható mezőgazdasági termelés peremfeltételeinek.

A harmonizációs folyamatoknak fontos része, az alkalmazott módszerek hátterének megismerése és egy olyan módszertan kidolgozása mely segít összehasonlítani és értelmezni a különböző talajvizsgálatok eredményeit.

Jelen dolgozatban a magyarországi talajvizsgálati módszereket az AL (ammónium-laktát), a KCl (kálium-klorid), a KCl-EDTA (kálium-klorid-etilén-diamin-tetraecetsav) hasonlítottunk össze a Mehlich 3, a vízes extrakció, (CoHex) kobalt-hexamin és az XRF (röntgen fluoreszencia) módszrekkel. Összehasonlító elemzéseink során foszfor-, magnézium -és cink- méréseket végeztünk 70 magyarországi talajmintán.

Az adatok elemzése során először a teljes adathalmazt vetettük össze, majd megvizsgáltuk a kálcium-karbonát, a pH, az Arany-féle kötöttség és az agyagtartalom hatásait. Következtetésként elmondhatjuk, hogy az általunk alkalmazott extrakciós-módszerek, a kiválasztott osztályozási módszerek és a statisztikai elemzések (minden adatot vagy bizonyos csoportot vizsgálva) is hatással vannak a foszfor, magnézium és cink mérésekre. Ezzel disszertációm olyan összehasonlító-elemző tanulmány is egyben, amely útmutatást nyújthat a különböző talajvizsgálati eljárások értelmezéséhez, a harmonizáció útján.

1. Introduction

Soil is an essential resource and a vital part of the natural environment from which most of the global food is produced. At the same time, soil provides the living space for humans, as well as essential ecosystem services which are important for water regulation and supply, climate regulation, biodiversity conservation, carbon sequestration and cultural services. However, soils are under pressure because of higher demands for food and competing land uses caused by population increase. (LAL 2008; KOPITKE ET AL., 2019)

Approximately 33% of our global soils are degraded (FAO and ITPS 2015; IPBES 2018). Policymakers are exploring opportunities to embrace sustainable development via sustainable development goals. Although the importance of soils seems clear, it has not received due attention in terms of their use and management, since soils were often considered an infinite resource that will always be able to provide us with its ecosystem services. However, this is not the case and **there is an urgent need to raise public awareness on the importance of soil, especially the need of protecting soils and using sustainably (FAO,** GLOBAL SOIL PARTNERSHIP**).**

Developing a strategy to maintain or improve soil fertility, is challenging for the farming communities. To harmonize the preservation of soil fertility with farming objectives there is a need for proper soil nutrient management strategies. These strategies should be based on data-driven information on the current status of the fertility of the soil. **Hence, the soil analysis is a valuable tool in the management of costs, it**

contributes to optimizing inputs while taking into account environmental and sustainability concerns.

Large soil databases including soil analysis results have been established in many countries in the past decades. However, the differences in historical backgrounds of the countries, together with varieties of soil, climate, plant species and differences in the systems of agricultural production led to **various soil testing procedures**. One of the greatest difficulties is interpreting their results due to the different methodologies applied in different countries and laboratories. It can thus be said that each analytical method is speaking "different languages" (SILANAPAA 1982).

Numerous methods are used for soil analysis around the world and even in the European Union. In the European Union, the Soil Protection Act makes it mandatory for farmers to monitor and maintain the fertility of their land and to base nutrient management schemes on soil tests, which is also a precondition for obtaining EU funds. Due to this, the regular testing of agricultural lands has become common practice. **Notwithstanding the mandatory soil sampling, the situation of soil analysis methods is very complex in Europe because there is no common regulation in analytical procedures of soil analysis** (HOUBA et al., 1992).

Soils can only be managed sustainably at the global and EU level if sufficient, reliable and comparable information becomes available. Harmonization of methods, measurements and indicators for the sustainable management and protection of soil resources is increasingly important to comply with the tightening legislation and boundary conditions for sustainable agricultural production.

In 2017, an initiative for harmonizing soil analytical data and methods has started by FAO, Soil Global Partnership.

***'Soils: if you cannot measure it, you cannot manage it'* (**FAO GLOSOLAN**)**

'The Global Soil Laboratory Network (GLOSOLAN) was established in 2017 to build and strengthen the capacity of laboratories in soil analysis and to respond to the need for harmonizing soil analytical data and methods. GLOSOLAN is working to improve the proficiency of soil laboratories in soil analysis, in both wet and dry chemistry (soil spectroscopy).

Harmonization of methods, units, data and information is critical to (1) provide **reliable and comparable information** between the countries and the projects; (2) allow the generation of **new harmonized soil data sets**; and (3) support for sustainable soil management' (FAO, GLOBAL SOIL PARTNERSHIP).

As we see there are several methods used worldwide and information about the different analysis methods should first be gathered in a harmonized way to compare the results and share experiences.

This thesis aims to summarize the Hungarian soil analysis methods that have a background from decades of work and compare them with other internationally used methods.

2. Aims and objectives

- The general aim is to compare the Hungarian soil analysis methods with international methods that might open new perspectives for the Hungarian laboratory analysis methodology.

- The study aims to compare the extraction efficiency of some widespread soil analysis methods (AL (Ammonium lactate), KCl (potassium chloride), KCl-EDTA (potassium chloride ethylenediaminetetraacetic acid) methods with Mehlich 3, water extraction, CoHex (cobalt hexamine) and XRF (X-ray fluorescence)) for phosphorus, magnesium and zinc measurements. An additional aim is to quantify the role of soil properties affecting extraction efficiency.

- In addition, to examine the different extraction methods, the impact of the classification of the influencing soil parameters and the statistical analyses (measuring all data or certain classes) were investigated, in the light of how these affect the evaluation of the results of soil phosphorus, magnesium and zinc measurements.

3. Literature review

3.1 PAST-PRESENT-FUTURE in the Hungarian soil analyses methods

3.1.1 Introduction

„*The higher culture developed and with it, the rational exploitation of the soil's fertility, more profound knowledge was gained by man about the qualities of soil through practice. Then at last - since Liebig -, it has become common knowledge of what role the soil's mineral composition plays in plantlife nutrition, first of all, chemistry took up soil examination, in hopes of creating an aid through chemical analysis, that would benefit agricultural practice. There was one route of soil examination that - through plant physiology and chemistry - led to the scientific knowledge of soil."* (INKEY 1914).

In our rapidly developing world, we are prone to forget our past, our great ones. This chapter on the one hand brings back the work of the determining individuals of this area of science, on the other hand, it draws the attention of the present's professional public opinion to several forgotten, but basic correlations. It does so in order for us to be able to reasonably and superbly employ achievements of techniques and technology. As it is apparent from the description of the past, domestic soil examinations go back several decades and parallel to that, our nutrition-management advisory also has great traditions. Even in this day, we can learn a lot from the past's experiences, reasonable and proper agricultural practices.

The judgment methods and utilization of soil examination have changed a lot. I would like to schematically review the works of some outstanding representatives of Hungarian soil studies and agrochemistry that represent the chain links of the development of domestic soil examination, all the way to the division of unified accredited soil examinations. In 1979 the Kék Könyv („Blue Book”) was published by MÉM-NAK (Plant Protection and Agrochemical Center of the Ministry of Agriculture and Food) (ANTAL ET AL., 1979; BUZÁS ET AL., 1979). To this day, it is the cornerstone of the advisory framework upon which domestic nutrient management has been based for the last 40 years. Already the second generation of farmers will base their nutrient management plans on it. There have been initiatives for the transformation of the professional advisory systems (ProPlanta, 3RP), but we may agree that the methods of soil analysis processes have hardly changed in the past decades in Hungary, at most the utilization of certain modern instrumental analytic detecting methods has become commonplace.

With the progress of digitalization, we may think that we are witnessing the renaissance of nutrient-management, but through the historical review, it is apparent that progress is not inevitably linear. Our existing soil analysis system provides well utilizable results to this day, however - following international trends – the domestic adaptation of novel soil analysis methods may provide new perspectives in domestic soil analysis and methodology of nutrient-management.

I find it important to review our well-founded science area that is rooted in the past, since we can only honestly judge and further develop today’s practical methods if we know it antecedents the past.

3.1.2 The Past of the Hungarian soil anlysis

3.1.2.1 The beginnings – early 19th century

In the 19th century Hungary, landowners were the most influential ruling class both historically and politically, with the development of agriculture as their primary interest. For this purpose, the state created a first-class research association by European standards in the 19th century and maintained it rather generously. Analyzing the domestic history of chemistry, SZABADVÁRY and SZŐKEFALVI (1972) emphasize that alongside the Prussian-style development, there was hardly any industrial research in the second half of the 19th century, but at the same time, an exceptional state research-institutional network was in operation, with agriculture as its sole branch. The results of said research profited large estates almost exclusively, landowners shifted the expenses of the research needed for international market competitiveness off to the state. This factor primarily benefited the development of agricultural chemistry. (KÁDÁR 1997).

3.1.2.2 The first agro-geological records

The Magyar Gazdasági Egyesület (Hungarian Economic Association) launched the process of discovering Hungarian soils in 1858. , *For the economical description of Hungary, among others, the study of geological conditions needs to be permitted, and that the Association conducts this through the dispatch of one or another geologist to the locale regarding every county, whose task would be the collection of available assorted kinds of soils for the implementation of physical and chemical examination.*’ The one who implemented the first true soil mapping in assorted regions of the country was **József Szabó** (SZABÓ 1867). He did this with the conviction that the regular study of the soil will benefit agriculture. This specialist started his work based on geology. He supplemented his soil record data with compositional diagnosis of soil sample solution gained through the usual process used in exploration of rocks. (BALLENEGGER and FINÁLY 1963).

Laboratory soil analyses were carried out in Magyaróvár also, at one of the main state institutes of plant cultivation experiments. (INKEY 1914). Agro-geologist Pál Treitz completed the soil maps of the Mosonmagyaróvár area as well as the experimental areas in 1892. They surveyed the fields of other state agricultural educational institutions for a similar reason: Inkey mapped the Pallag estate of the Debrecen educational institution in 1892 (INKEY 1897a); Treitz collected records in Keszthely in 1897 and in Kassa in 1899 (TREITZ 1901). The agro-geological records of larger state-owned estates were created at this time too, since they conducted important plant cultivation experiments on these estates, thus it was imperative that they discover the soil conditions and chemical qualities of these areas.

The Mezőhegyes stud estate was mapped in 1893 by INKEY (1898a, b), the Bábolna one in 1900 by HORUSITZKY (1902), the Gödöllő crown estate in 1906 by TIMKÓ (1909), and the Kisbér stud estate in 1912 by HORUSITZKY. The soil analysis work conducted at experimental stations and also production experiments carried out there were summarized in reports (KOSUTÁNY 1890; VEDRŐDI 1890; GÁSPÁR 1897; KÖNYÖKI 1898; SOMSSICH 1898; CSERHÁTI 1900a; SIGMOND 1901a, b, 1906).

For the first time, SPORZON (1865) summarized contemporary knowledge in connection with soil, soil examinations and soil fertility in general, in Hungarian language as an independent study book titled „Agricultural soil knowledge, that is, the infield" (KÁDÁR 1997).

3.1.2.3 The first soil examination methods

At first soil researchers were endeavoring to gain the data about quantity of the soil's valuable materials by the use of hot concentrated hydrochloric acid. KALECSINSZKY (1883) while carrying out the chemical study the Alsótátrafüred bog soil, specified the components of the soil soluble in water, alcohol, light soda solution, light potassium-hydroxide solution and light hydrochloric acid solution, respectively. VEDRŐDI (1890) specified components soluble in concentrated hydrochloric acid in Pallag soil. Interesting to note that already in 1894, Inkey objected to this method of exploration. In his opinion, what needed to be specified was not the soil's complete, but rather "ready" nutrients' quantity, for which he recommended the use of a simple water extract or extracts made with lightly carbonated water or perhaps thin solutions of organic acids. (INKEY 1897a, b).

BITTÓ (1897b) reported data about the calcium and magnesium content of domestic soils, tagged by the following notice: '*to draw conclusions about the production condition of the examined soil or about what kind and quantity of fertilizer we should use solely based on these numbers is utter impossibility, because the numbers showing the result of the analysis do not inform at all about in what condition does the soil contain individual components and how much plants are able to absorb from those...*'.

3.1.2.4 The Cserháti School

By the end of the 19th century, the first, truly science-driven (at least according to the present definition) soil fertility researches are tied to the work of the Cserháti School. According to their view, we can only inform ourselves about the soil's nutrient condition exclusively through open-ground experiments, because soil analysis can't predict absorbable nutrient elements. The skepticism of Cserháti is understandable since as we mentioned before, most contemporary soil analysis methods used relatively thick acids and alkalis as solvents with which we can rather inform about the "raw" nutrient stock of the soil, not its "soil power". Cserháti thought that soil analysis can only provide answers about given nutrient's existence or absence. Only plants can give us an answer about how many absorbable and explorable nutrients there are. (CSERHÁTI and KOSUTÁNY 1887, CSERHÁTI 1900b).

At the end of the 19th century, CSERHÁTI and KOSUTÁNY (1887) summarize theoretical and practical results achieved in the field of plant nutrition most comprehensively in their books titled Basics of Fertilizing and Plant Cultivation (CSERHÁTI 1900c).

3.1.2.5 The work of Elek Sigmond

SIGMOND (1901a, b, 1904, 1906a, b, 1910a, 1934, 1938a, 1938b) was the most significant developer of Cserháti School, his agrochemical work's central issue is soil examination, the specification of the soil's absorbable P content (Sigmond 1900, 1901a, 1906a, 1907). His method, where easily absorbed phosphoric acid is dissolved from the soil with thin nitric acid, and where the soil's reaction is also taken into consideration

(Sigmond 1906a), had become general use by 1906, in 1928 Becker also successfully utilized it for specifying easily absorbable potassium content (Becker 1928). He also studied the phosphoric acid fertilizer requirement of the soil (Sigmond 1901a, b), and methods for determining soil fertilizer requirements in general and also, data evaluation. (Sigmond 1908, 1910b, 1909, 1914a, b, 1914c, 1914d, 1915, 1924, 1927a, 1927b, Sigmond et al. 1927a). Sigmond emphasizes however, that soil examination is not a substitute for exact field experiments, both tools are needed for fertilization control. In his view, the yield is related to the amount of easily soluble nutrient in the soil, but this correlation is not "one-sided", because it is influenced by a number of other factors. Among these factors, he highlighted the soil: '*Researchers should take the different dynamics of soil types into account, adapt the threshold values, and evaluate analytical data accordingly. There would be much less contradiction and conclusions would be more certain if they did not look for the thresholds of practical requirements in general, but rather by soil type'. This is clearly demonstrated by the fact that the threshold values successfully applied by some researchers in a narrower area are no longer applicable in other, dissimilar types of soil regions*.' The available test material did not allow Sigmond to refine the nutrient supply threshold limits by soil type, but did so by degrees of alkalinity. As the lime content of the soil increases, so does the amount of phosphorus soluble in dilute nitric acid, although this does not actually improve the phosphorus supply to the plant. The threshold limits are therefore higher on calcareous soils. Sigmond's work was continued by his two most important students, Várallyay Sr. and Dworák.

3.1.2.6 Ballenegger: Book of Soil Analysis Methodology

Ballenegger reported on the nutrient stock of soil types in Hungary in 1914 (BALLENEGGER 1914a, b), then following that he described the chemical composition of different Hungarian soils (BALLENEGGER 1916a, b, 1917a, b, 1926) and the nutrient salts of the soil (BALLENEGGER 1920, 1921, 1923). Edited by him, the Book of Soil Analysis Methodology was published in 1944 (BALLENEGGER and MADOS 1944). For the first time, it summarizes and describes in detail about the laboratory test methods that may be recommended for use in soil examination, as well as the outdoors soil recording procedures, and also provides information on the practical evaluation of test results. Ballenegger summarized the chemical, physical, and biological soil testing methods studied by researchers of the age. In his soil testing methodology book, Ballanegger mentions methods studied by several researchers. I would like to schematically summarize the physical and chemical test methods described and studied at the time.

Methods of mechanical soil testing:

- Atterberg's elutriation method was used and described by Róbert Ballenegger to determine the mechanical composition of Hungarian soil types (BALLENEGGER 1915).
- For the simple and fast specification of soil plasticity, Arany developed a procedure (ARANY 1943), which is still commonly used by our soil testing laboratories according to the standard MSZ-08-0205: 1978. KLÉH and STEFANOVITS (1943) dealt with the soil’s classification according to state of soil plasticity.
- Sigmond wrote about the benefits of mineralogical soil analysis (1934) and data was reported by Vendl (1914).

- BALLENEGGER (1915), BOTVAY (1937, 1940), SCHUMACHER (1935), GÜLL (1906), HORUSITCZKY (1907), MADOS (1939), PREISICH (1942), ROMWALTER (1935), SIGMOND (1916), TREITZ (1900) and VÁRALLYAY SR. (1938) dealt with the mechanical analysis of soils from a methodological point of view.

Methods of the soil's chemical examination:

- BALLENEGGER (1916b), HILGARD (1910) address the methodological issues of preparing the **hydrochloric acid** extract, and SIGMOND (1907b, 1909, 1911, 1912, 1914a, 1914c, 1914d, 1924, 1927b, 1927c 1935) does so particularly, whose procedure has also been accepted for international use. In Hungary, the dilute nitric acid method spread 'SIGMOND (1901, 1929)
- Ballenegger used the hydrochloric acid extract of the soil for the chemical characterization of the main soil types of Hungary by complete segment tests. (BALLENEGGER 1914a, b, 1916a, b, 1917b).
- To characterize the chemical composition of the soil, our researchers also used the composition of the **aqueous extract** of the soil. Ballenegger had shown that the composition of the soil's aqueous extract does good service by the characterization of our soil types (BALLANEGGER 1913a, 1913b). ARANY (1928), BALLENEGGER (1913b), KOTZMANN (1933) and SCHAY (1927) discussed the methodological issues of the aqueous extract.
- Several dissertations are about the physico-chemical and chemical processes of **base exchange**. The soil's base-binding and -

replacing ability, the chemical nature of the bound bases and their proportion to each other are important characteristics of the soil’s chemical state and play a fundamental role in the modern characterization of certain soil types; it is one of **Sigmond's soil classification system’s basic criteria** (SIGMOND 1934). ARANY (1933), BUZÁGH (1943), CSIKY (1932), DI GLÉRIA (1929a, 1929b, 1936), KOTZMANN (1928, 1935), MADOS (1942, 1943), SÍK AND ZAKAIRÁS (1933), Sigmond (SIGMOND and DI GLÉRIA 1927b, 1927c; SIGMOND 1933; SIGMOND and IYENGAR, N A. S. 1934-35), VAJNA (1929) addressed these issues in detail.

- SIGMOND (1927e, 1927a, 1935, 1936, 1938b) dealt with the chemical characteristics of soil leaching.
- ENDRÉDY (1931, 1941) developed a method for specifying certain components, such as potassium. HORVÁTH (1914, 1916) examined the specification of manganese and silicon content in the soil.
- DWORAK (1928), KÜHN (1928) and TREITZ (1903, 1904, 1910) proposed a new method for the specification of **carbonated lime**.
- ARANY (1931), BITTÓ (1897a, b) HERKE (1929) dealt with the calcium and magnesium content of soils.
- DI GLÉRIA developed a **dialysis procedure** to determine the soils’ nutrient content (DI GLÉRIA 1930).
- Kühn recommended an **ammonium carbonate solution** for the extraction of nutrients (KÜHN 1935).
- PRETTENHOFFER (1936) examined the possibilities of determining the soil’s potassium requirements by the use of **ammonium chloride solution**.

- At the time there was little domestic experience about the Egnér procedure, but it was successfully used abroad for mass testing (BALLENEGGER and MADOS 1944). **During the Egnér procedure** (EGNÉR 1940) the specification of easily soluble potassium and phosphorus is conducted with a calcium lactate solution of hydrochloric acid of a prescribed composition (RIEHM 1938; RHEINWALD and CONSTANTIN al. 1939).
- KOTZMANN (1928, 1935), SÍK (1941) and WITKOWSZKY (1942) wrote about the specification of the soil's organic material (humus).
- PÁTER (1929) dealt with the C/N ratio of organic matter, VÁGI and FEHÉR (1931) wrote about the formation of organic matter.

3.1.2.7 The work of György Várallyay Sr.

As we can see, they researched numerous examination methods, but of the Sigmond disciples, VÁRALLYAY SR. (1950, 1954) and DWORÁK (1930, 1934) were the ones who primarily carried on the "Sigmond school" and worked very effectively to clarify the correlations between soil examination data and fertilizer effects.

Interest in soil analysis was gradually increasing, and from the 1920s, they conduct analyses to manage soil improvement and fertilization at more and more sites in Hungary. In the early 1930s, the first large-scale fertilization experimental operation combined with soil examinations was launched. The study of the correlations between fertilizer effect and soil examination data did not lead to direct positive results -said Várallyai Sr. -, but it did provide a number of lessons for the participating researchers. The analysis of the causes of lack of results has made progress possible, to move forward, the elimination of theoretical and methodological ambiguities (KÁDÁR 2015).

Between the two world wars, the rye seedling method recommended by NEUBAUER and SCHNEIDER (1923) similar to many European countries, was widely used in Hungary, to assess the nutrient supply of soils. The method gave a general supply threshold regardless of the soil, below which a fertilizer effect is expected, but not above it. This one-plane correlation was not confirmed in field experiments between the years 1932-36 (KÁDÁR 2015).

During the studies, several chemical and biological methods used at that time (LEMMERMANN (1925, 1930), Azotobacter, Aspergillus etc.) were compared with the accepted standard Neubauer test of plant physiology: *"...We looked at how the individual methods match each other, while we lost sight of the main goal, the correlation between soil examination and fertilizer effect.*" VÁRALLYAY SR. (1954) concluded that **a simple and fast chemical procedure is needed instead of testing without many repetitions. Namely, any method can be good, it just needs to be calibrated.** Later, for further studies, the DL method (RIEHM 1940, 1942) - suitable for rapid, serial testing - was selected. In addition, micro-dose fertilization and 18-day maturation laboratory examinations were performed on the samples, in order to obtain information - in addition to the soil’s DL-P content’s specification -, about the % change as a result of fertilization (filling-binding) (KÁDÁR 2015).

Várallyay refined the DL-PK thresholds for soil types and plants based on the data of the small-plot repeating classical deficiency experiments he had already initiated. The adsorption is moderate and the extraction capacity is more intense on calcareous sand and lime-rich chernozem soils, which is why the DL-P thresholds are higher here as well. However, they are lower on acidic brown forest soils, Danube alluvial soils and on acidic sandy soils. He refined DL-K thresholds for plant groups. (KÁDÁR 1997, 2015).

3.1.2.8 The 1950s and 1960s

However, after Várallyay Sr's death (1954), there was a break in development. There was no one who understood enough and took this work further. It was unfortunate, because in the period that followed, the possibilities expanded. New research institutes and soil testing laboratories were established, and fertilizer use multiplied. Although many agrochemists, such as SIK (1964), SIK and FÁBRYNÉ (1950), SIK and SCHÖNFELD (1952) achieved valuable partial methodological results, the momentum of the work subsided with the death of Várallyay. The number of fertilization experiments aimed at the study of fertilizer’s effects greatly decreased. The latter was also due to the spread of the William-Lysenko trend, which emphasized the role of soil structure and grass rotation at the expense of fertilization. (KÁDÁR 1997, 2015).

Sarkadi and his coworkers (SARKADI and KRÁMER 1961, 1966; SARKADI 1959; SARKADI et al., 1965, 1976; THAMNÉ et al., 1968) addressed the theoretical and methodological problems of estimating fertilizer demand in several of their works, and also proposed provisional thresholds for PK content that could be solved by the use of AL and DL methods, respectively. They pointed out that with the DL method previously used in Hungary we might significantly underestimate the P-supply of our soils in calcareous areas due to the secondary precipitation of P, therefore they proposed to switch to the AL method, where Ca-lactate is replaced by ammonium lactate as solvent, buffered to pH 3.7 (KÁDÁR 1997, 2015).

According to the research of RIEHM and WICHENS (1967), the pH value of the AL-extract is 5 even in soils with an approximately 30% $CaCO_3$ content, that is under the threshold value of $CaHPO_4$ precipitation. Several people, including the aforementioned authors, sought a correlation between the soil's lime status, pH value and soil examination data, and developed correction factors to convert DL values to AL values. The AL-P/DL-P ratio in carbonate free soils was 1:1,5, in soils with 2–10 % $CaCO_3$ content it was 1:2, above 10 % $CaCO_3$ content it occurred at approximately 1:4-5 (KÁDÁR 1997, 2015).

3.1.2.9 The 1970s, 1980s and the MÉM-NAK

In the 70's and 80's the work continued, that tried to clarify the roles of basic soil properties (lime state, cohesion, humus content) in the interpretation of soil examination thresholds

In 1976, the Mezőgazdaság és Élelmezésügyi Minisztérium (Ministry of Agriculture and Nutrition) issued an edict for the introduction of a new soil power management system that formulated the following main objectives:

- construction of fertilizer storage facilities to reduce direct fertilizer loss,
- construction of a modern, unified soil nutrient testing network,
- development and introduction of an expert counsel system based on the results of soil nutrient testing,

- establishment of a licensing system for fertilizers and other substances that have a positive effect on soil fertility.

A network of soil testing laboratories with a unified instrumentation and methodology was established in the country, with 15 laboratories. As a result of their work, the first soil testing cycle was completed in 1982 in the agriculturally cultivated areas of the country.

The capacity of one laboratory was 14-16 characteristics of 200 soil samples per day. With this performance, **it was possible to monitor areas every 3 years on average**. (BARANYAI et al., 1987).

At the development of the Hungarian uniform fertilization expert counsel, at the time of the **establishment of the MÉM NAK** (1976), the task of the Measurement Methodology Committee was to summarize the results for the expert counsel. Basic or background research in Hungary made it possible for the profession to satisfy the needs of the time and to offer uniform principles of expert counsel and methodology in a short time.

In micro element research TÖLGYESI (1969), KERESZTÉNY (1971), PAIS (1980), ELEK and KÁDÁR (1980), GYŐRI (1984); in estimating phosphorus demand FÜLEKY (1977), THAMMNÉ (1981), SARKADI et al. (1987); in the further development of the Mg methodology LOCH (1970); in the field of liming NYIRI (1986), BLASKÓ (1985) and BALOGH (1988); in the study of sandy soils' fertility, e.g. LÁSZTITY (1976), CSERNI (1982), SZEMES (1986) and others reported valuable soil analysis data in the past decades. The combined effect of potassium, calcium and magnesium fertilization was examined in detail by KOZÁK et al. (1983) on the sandy soil of Nyírség. Pál Stefanovits and his coworkers drew a map of clay mineral cenoses of domestic soils (STEFANOVITS, P and DOMBÓVÁRINÉ 1985), and developed the agricultural applications of the studies (STEFANOVITS, P., 1993).

The second volume of the Soil and Agrochemical Testing Methodology Book -edited by István Buzás-, was published in 1988. (Physico-chemical and chemical test methods for soils), followed by the first volume only in 1993, titled Soil and Agrochemical Test Methodology 1. (Physical, water management and mineralogical examination of the soil) (BUZÁS 1988, 1993). Géza Szendrei's monograph titled Soil Mineralogy (1995) discusses the role and distribution of minerals in determining soil properties.

The contents of the original Kék Könyv ("Blue Book") summarizing the essence of fertilization advice based on soil tests (ANTAL et al.,1979; BUZÁS et al., 1979) were published in many other places (DEBRECZENI B. 1979, BUZÁS I. 1983, ANTAL J. 1983, 1987, 2000). Under political pressure, the thresholds were changed in 1987 without the consent of the authors (in the so-called "white book"), but the fertilizer doses increased in such manner lack any scientific basis. Fortunately, the use of original thresholds became widespread and is still used today.

Initiatives to redesign expert counsel systems included the introduction of ProPlanta, which works with modified thresholds and a new calculation method based on the results of long-term experiments, or the expert counsel system called 3RP.

However, soil testing methods have not changed in recent decades, although following international trends, domestic researchers are constantly experimenting with the development or adaptation of new soil testing methods. The study of 0,01 M $CaCl_2$, an internationally known soil extractant, was started in 1990 by the staff of the then-called DATE Department of Agricultural Chemistry (BERTÁNÉ 2016). The 0,01 M calcium chloride solution is a significantly milder extractant, which mainly extracts the easily soluble and replaceable nutrient content. The introduction of a unified European method had already arisen in 1994. The necessary research started in several European countries, including the Department of Agricultural Chemistry of DATE in Hungary. The advantage of this method is that several nutrients can be measured from one extract, which also allows the specification of nutrient ratios (LOCH and JÁSZBERÉNYI 1997, HOUBA et al., 1991, JÁSZBERÉNYI et al., 1994, 1999).

3.1.3 The Present practice of soil analysis

One of the most important key elements in reviewing the past is that we can see how important soil analysis was as a part of nutrient management planning, sampling and examining soil every 3 years, drawing up operational soil maps. These days, although soil test results are available to farmers, in many cases there is a lack of evaluation of the results and field-level planning, or it happens solely to be adequate for official requirements, to comply with the Nitrates Regulation. Ignoring soil analysis results, the ’tis the way we do it’, that is the nutrient replenishment based on habits may not work properly, especially in extreme weather situations. Soil testing should be an important plant cultivation decision support tool in the hands of farmers. Knowledge of the current state of soils is essential when planning cultivation technology interventions. It is only possible to determine the date of the nutrient replenishment, the composition and the amount of the applied fertilizer in a well-founded way - as best adapted to the needs of the plants - if the nutrient supply of the soil is known. The shortest possible time should pass between measurement and intervention in order to truly take into account the current soil condition, **however, soil test results are often delayed for weeks due to the laboratories’ overload.**

It is also apparent that the methods of soil testing have hardly changed methodologically in Hungary in the last 30 years, although initiatives have been taken to alter the expert counsel systems.

The need to enhance test methods is fueled by several sources:

- One of the problems with the currently used expert counsel based on the AL-P, AL-K, and humus content is that the measured soil examination values are highly dependent on the physical and chemical properties of the soil. AL-P, AL-K are partly related to the % of humus and fully related to the amount of nutrient reserves (BERTÁNÉ SZABÓ 2016).
- The existing methods have been developed primarily for field cultivation. Intensive horticultural production - especially sheltered cultivation -, requires other types of expert counsel. (BERTÁNÉ SZABÓ 2016).
- We have known for a long time that there is no extractant that is suitable alone for the characterization of the processes taking place in the soil, nutrition element requirements can only be estimated. (SARKADI 1975).
- BUZÁS (1987) points out that in fact, it is not the amount of nutrients that should be measured, but rather the rate of formation of plant-absorbable nutrients from those that cannot be taken up.

- By using the described simple “dynamic” model - despite the constant transformations of soil nutrient element forms-, the concepts of “absorbable nutrient quantity”, nutrient stock, and nutrient supply can be clarified; concepts that have been used so far without being defined by anyone. Using the example of phosphorus, he proves by using simple mathematics, that complicated speed measurement is not necessary, because the absorbable nutrient content is proportional to the speed of the nutrient supply.
- According to LOCH (2006), one of the extractants should be suitable for specifying the amount of nutrients present in the soil solution, the other, more powerful solution should ensure the extraction of nutrients available for the plant's active nutrient uptake processes, that is easily mobilizable reserves (current and potential nutrient supply). AL solution used in Hungarian expert counseling is a strong extractant. Based on the experience of decades of use, several authors (LOCH et al., 2005; KOCSIS 2005; FEKETE et al., 1983; MARTH 1990; FÜLEKY 1999) have suggested expanding the range of soil extractants.
- Different extraction agents have been standardized in individual European countries, for example in the Netherlands a mixture of 0,1 M HCl+0,2 M oxalic acid is used to determine K, while phosphorus is determined in water or AL at 20 °C, depending on whether it is to do with ploughland or grassland. In the second half of the last century, with the development of analytical methods, the use of mild extractants (distilled water, dilute saline solutions) came to the front, as presumably the amount of

nutrients soluble in them well characterizes the currently available nutrient content (LOCH 2006).

- Extraction with acidic saline solutions, such as AL - which is also used in Hungary - or DL also dissolves some of the reserve stocks, so with these methods we obtain a so-called capacity parameter (HOUBA et al., 1991, FOTYMA et al., 1998).
- BUZÁS (2012) reviewed publications on soil testing in 60 years of the journal Agrochemistry and Soil Science published up to that point in time. He introduced the concept of merit of soil tests, their necessaries and sufficient conditions. He concluded that over time, less aggressive extractants were becoming prevalent in the development of soil testing. The natural reason for this is that efforts are being made to reduce the dependence of soil test results on soil types. He proved that dependence on soil types is small if the amount of nutrient extracted is proportional to the amount of absorbable nutrient form that is present in small amounts in the soil sample, rather than to the total nutrient content of the soil sample. This is only possible if weak extractants are used, that release small amounts of nutrients (see also BUZÁS 1987).
- The current test methods mean traditional laboratory tests, that is the soil samples are analyzed in a test laboratory after the necessary sample preparation procedures - drying, grinding -, almost exclusively by wet exploration. During which, a set amount of extractant solution is added to a given amount of soil. During standardized (up to 1-2 hours) shaking, nutrients in the soil are dissolved by the effect of the solvents. Each nutrient is

specified from soil extracts using a suitable instrumental analytical detection method. It is also clear from the description that the method is time consuming and chemical intensive (DORKA-VONA et al., 2019).

- During the current standardized soil tests in Hungary, different extractants are used: phosphorus and potassium are specified with ammonium lactate, magnesium with potassium chloride, while magnesium is specified in EDTA-KCl solution, so several extractions must be performed to specify them. (DORKA-VONA et al., 2019).
- In case of elements that can be specified in one solution, the interactions between the individual elements (synergism, antagonism) are more observable than in cases where different extractants are used.
- Several new, faster methods have emerged for more accurate texture specification,
- It is difficult to integrate the Arany's type plasticity index into international growth models. Multinational companies use clay percentage in the variety proposal and in determining variable seeding, planting.
- By the specification of humus, a large amount of concentrated acid is still used and the problem of CrVI is even more significant.
- Current methods are time consuming and labor intensive.
- The question arises as to what other parameters could be used to make the expert counsel even more precise? (e.g. examination of biological parameters)

3.1.4 The Future perspectives of soil analysis methods

In the digital world of the 21st century, smart devices and sensors play an increasingly important role in farming. The need to adapt to extreme weather events poses new challenges for farmers, since providing the right answers in a timely manner is one of the cornerstones to climate-adaptive farming. Smart, rational management, the use of information and data technologies to optimize complex management systems is unavoidable. The nutrient content of the soil is currently specified by the conventional solvent extraction laboratory test method. This method is known, recognized and standardized for the profession, but it should be noted that in the last decade there has also been a need to develop new measurement methods and technologies. The vast majority of soil nutrient testing methods are so-called dissolution methods, but other methods have also been studied in Hungary, such as the Chaminade method (SÁRDI 2001; SÁRDI and CSATHÓ, 2002), the infrared spectroscopic procedure (TÖRÖK 1972a), the x-ray induction analysis (PÁRTAY 1980; PÁRTAY and SZENDREI 1981), the algae test method (ÖRDÖG and MÁTÉ 2002).

Of the various methods, perhaps the most important are the **spectrometric methods**, which have been used for a long time in various sectors. As an example, near-infrared (NIR) spectroscopy has been a widespread method for almost 40 years, typically used in the field of pharmaceutical production and medical diagnostics, as well as in food quality control processes and feed testing.

In recent decades however, the study of the pedological applicability of spectrometry has gained an increasingly important role. Over time, spectrometric methods may be promising alternatives to replace or supplement traditional laboratory methods in the future. These techniques are faster and require little or no chemicals and are therefore able to offer a fast, affordable solution and can even be performed in field conditions. (VISCARRA et al., 2006, COHEN et al., 2005).

Spectrometric methods are considered to be an indirect method as opposed to the direct approach of traditional wet chemical methods, since during spectroscopy the values of each parameter are obtained from the spectral absorption curve of the soil sample. The basis of spectroscopic measuring is that each soil component absorbs or reflects infrared rays back to a certain extent. The data of the mapped absorption curves are entered into a database, from which algorithms calculate the pedological parameters of the given sample using chemometry (multivariate, multidimensional data analysis). The algorithms (predictive models) use all the data in the database (VISCARRA et al., 2006, DANIEL et al., 2003). Predictive models examine the peaks and slopes of the spectrum of a given soil sample and then compare them with adjacent spectra that show similarity to the respective spectrum. Through the information obtained from the examined spectrum and the adjacent calibration spectra, we receive the best possible estimate. One of the major challenges of reflectance spectroscopy's application in soil analysis is the calibration and validation of the method. Through this, the basic task is to collect calibration soil samples and to create reliable calibration models that compare the spectra of the soils with their laboratory results. (SORIANO-DISLA et al., 2014). The development and testing of procedures that enable fast, real-time measurements - which are also a breakthrough for fast paced, precision farming -, is currently underway.

3.2 The ‘Babel’ of soil analysis methods – international outlook

The availability of chemical elements from soils to plants, and ultimately to animals consuming them, has been studied by scientists for centuries (BAKER 1990). Scientists have been developing several methods for determining plant-available nutrients in the soil (RAUN et al., 1998).

LIEBIG (1840) was an early worker in the soil-testing field. From Liebig's time in 1850, until the early 1920s, little progress was made DYER (1894), HILGARD (1911), and BURD (1918) made significant contributions to soil chemistry. These early soil analyses were dominated by total analysis, using strong extraction solutions. During the late 1920s and early 1930s, remarkable contributions to soil testing were made by BRAY (1929), HESTER (1934), MORGAN (1932), SPURWAY (1932), and TRUOG (1930). These scientists emphasized the importance of measuring labile instead of total soil nutrient content. Since the late 1940s, soil testing has been widely accepted as an essential tool to formulate a sound lime and fertilizer program. (PECK 1990)

An outstanding progress has been made during the last century worldwide in many respects, including a scientific understanding of soil chemistry and soil-plant relations, soil sampling, analytical instruments and methods, data processing and quality control. (VAN RAIJ 1998; JONES 1998). Today soil testing is the most widely used chemical analysis performed in agriculture (VAN RAIJ 1998).

However, a large number of extractants are used in routine soil testing, often without the standardization of the method. The main reason for the existence of a large number of approaches and methods used in soil testing is the complexity of soil chemistry and the soil-plant relationship (VAN RAIJ 1998).

A good example of the variety of soil testing procedures is presented in Table 1. A list of extractants, published by, HOUBA et al., (1992) shows numerous methods being used for different plant-available nutrients in different parts of Europe and other countries. JONES 1973 published similar variations in soi testing methods. He prepared a summary of soil testing methods used in all the state-operated laboratories in the USA. Just for plant-available phosphorus (P) there were ten different extraction procedures, and nine for plant-available potassium.

Table 1: Extraction procedures of potassium soil by country (Houba 1990)

Country	Solution	Ratio	Time	Other Elements
Austria A	IM ammonium acetate	1:20	90 min	Na, Mg, Mn, K
Austria B	Calcium acetate lactate (CAL)		120 min	K
Austria C	EUF	1:20	0-30,30-35 min.	NO_3, NH4, Al, Na, K, Mg, Ca, P
Belgium	Ammonium lactate/acetic acid (pH=3.75)	1:20	240 min.	Ca, Mg, Na, P, K
Finland	0.5M CH_3COOH +0.05M CH_3COONH_4 (pH=4.65)	1:10	60 min	Mg, K
France	IM amonium acetate	1:20	60 min	Na, Ca, Mg, K
Germany A	Double lactate or calcium ammonium lactate			K
Germany B	EUF		0-30,30-35 min	NO_3, HH_4, Al, Na, K, Mg, Ca, P
Great Britain A	$1MNH_4HO_3$	1:10	30 min.	Mg, K
Great Britain B	IM ammonium acetate		150 min	K
Great Britain C	IM ammonium acetate	1:10	30 min.	Mg, K
Hungary	Ammonium lactate/acetic acid (pH=3.75)	1:20	120 min	K
Ireland	Sodium acetate/acetic acid (Morgan's solution)		30 min.	K, P, Mg
Netherlands	0.1MHC1 + 0.2M oxalic acid	1:10	120 min	K, Na
Portugal	ammonium lactate/acetic acid (pH=3.75)	1:20	120 min.	K
Spain	IM ammonium acetate		60 min.	K, Na, Mg
Sweden	ammonium lactate/acetic acid (pH=3.75)	1:20	90 min	K, Mg

An example of the methods used for the determination of "available" potassium in soils is given in Table 1. The table shows that ammonium salts are the most frequently used for available potassium determination, but differences in extraction procedures are rather important. Shaking ratios vary from 1:2.5 to 1:20, and shaking or percolation times from five minutes to six hours. Efforts to increase the efficiency of the procedure are made too. In some cases, a number of other nutrients, not only cations, are determined in the same extract (Houba 1990).

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3.3 The 'quantity'/'intensity' approach in soil analysis

SCHOFIELD (1955) distinguished two nutrient fractions in the soil:

- the 'quantity,' indicating the amount of potentially available nutrients,
- and the 'intensity,' indicating the strength of nutrient retention.

The **'quantity'** reflects all the nutrients within or adsorbed at the soil constituents, while the **'intensity'** reflects the nutrient concentration in the soil solution. The 'intensity' and 'quantity' are interrelated by the buffering capacity of the soil, which is an indicator of the capability to maintain a certain nutrient concentration in the solution (MENGEL and KIRKBY, 2001) The 'quantity'/'intensity' approach is valuable for nutrients like phosphorus and potassium (HOLFORD 1991; HOLFORD and DOYLE, 1992; EVANGELOU et al., 1994; RAVEN and HOSSNER, 1994), but cannot easily be applied to nutrients predominantly in organic forms and/or to the nutrients that are hardly buffered by soil constituents. Due to fertilization, nutrient uptake by crops and mineralization, the concentration of (non-buffered) nutrients in the soil solution may vary enormously (YANAI et al., 1996).

3.3.1 Intensity approach

The rate of nutrient uptake rate by plant roots is positively correlated with the nutrient concentration in the soil solution (NYE and TINKER 1977; BARBER 1984), i.e., with the **'intensity'**. Hence, the nutrient concentration in soil solution may be a representative indicator of the actual nutrient availability in the soil. The methods that are developed to separate the soil solution from soil constituents (DAHLGREN 1993; JONES and EDWARDS 1993; LORENZ et al., 1994; LAWRENCE and DAVID 1996) do not always provide information on actual concentrations because the soil solution may be altered substantially during the separation process. Nevertheless, water or dilute salts are widely used as extraction solutions to assess the nutrient concentration in soil solution (HOUBA et al., 1990; DAHLGREN 1993). In case of the application of these weak extractants, the amounts of extracted nutrients heavily dependent on e.g., sample drying temperature and sample storage (BARLETT and JAMES 1980; HOUBA et al., 1989, 1995; RECHCIGL et al., 1992), soil: solution ratio, shaking time (REZAIAN et al., 1992) and extraction temperature (HOUBA et al., 1989). '*Results of soil extraction with water or dilute salt solutions are probably related, but certainly not equal to the actual nutrient concentration in the soil solution. Interpretation, the quality of soil testing programs may improve if the soil chemical processes that determine the nutrient release during the extraction process are taken into account'* (VAN ERP 2002).

3.3.2 Quantity approach

The 'quantity' is determined by using total elemental analysis. From a crop nutritional point of view, the application of these total analysis methods are limited because only a very small fraction of the total reserve can be taken up by the crop during one growing period (VAN ERP 2002). From nutrient management aspects, the estimation of the size of the 'labile' (MARSCHNER 1995) pool may be a better indicator of nutrient availability. Determining this 'labile' pool', the combination of acids, hydroxides, complexing agents or salt solutions are used as extractants (FIXEN and GROVE, 1990; HABY et al., 1990).

Ion-exchange resins (RUBAEK and SIBBESEN 1993) or ion-exchange membranes (QIAN et al., 1992) are also used sometimes to determine the size of the 'labile' nutrient pool.

‘The theoretical foundation of the functioning of most extractants is well known, but it is difficult to use this knowledge for selecting an extractant because the chemical binding forms of nutrients in the soil are mostly unknown’ (VAN ERP 2002). Generally, nutrients associated with the cation exchange complex are extracted with high molar salt solutions (HABY et al., 1990; MEYER and ARP 1994). To extract nutrients presented in minerals with a low solubility product, or in minerals from which the release is kinetically restricted, acids or hydroxides, resins or other nutrient-specific methods are used (Figure 1) (FIXEN and GROVE 1990; MENON et al., 1997).

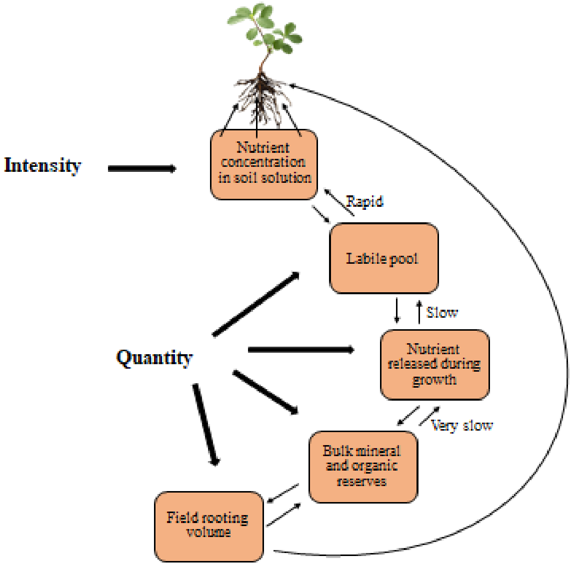
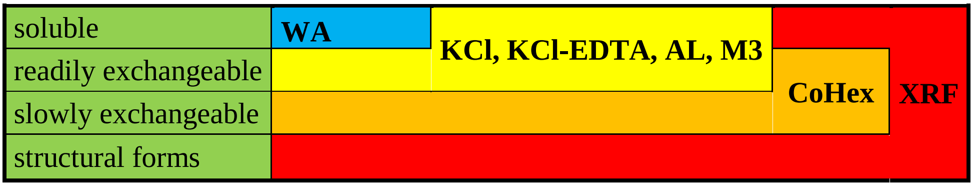


Figure 1: Intensity, quantity and nutrient sources (after Williems 1970)

3.4 Background of the extraction methods in the study

As it was written in the previous chapter, plant nutrients exist in many different forms, or **nutrient pools**, within the soil. These pools range from soluble, readily available forms, to weakly bound forms that are in rapid equilibrium with soluble pools, to strongly bound or precipitated forms that are very insoluble and become available only over long periods (BIERMAN 2005). Different extraction methods are developed to measure the nutrients in the different pools.

Extractants are solutions, that separate nutrients from the sorption complex. Hence, the extractant increases the concentration of a specific element in the solution which can subsequently be detected by laboratory equipment. Extractants differ in their strength, a weak extractant represents the readily available pool of certain nutrients, whereas a very strong reagent represents a more stable pool of that nutrient (Figure 2) (VAN ERP 2002).



soluble	**WA**	**KCl, KCl-EDTA, AL, M3**		**XRF**
readily exchangeable			**CoHex**	
slowly exchangeable				
structural forms				

WA – Water extraction, KCl – Potassium Chloride, KCl-EDTA – potassium chloride-EDTA, AL – Ammonium lactate, M3 – Mehlich 3, CoHex – Cobalt hexamine, XRF – X-ray fluorescence

Figure 2: Nutrient forms in soil and extraction methods.

The water extraction method (WA) is mostly used to measure the soluble form of nutrients (WUENSCHER et al., 2015). The Potassium Chloride (KCl) (LOCH 1970), potassium chloride-EDTA (KCl-EDTA) (MÉM-NAK

1978; BARANYAI et al., 1987; SZŰCS et al., 2003), Mehlich 3 (M3) (MEHLICH 1984) and Ammonium lactate (AL) (NOVOZAMSKY and HOUBA 1987) extractants are considered to measure the soluble and readily exchangeable forms. With Cobalt hexamine trichloride (CoHex) method, the readily and slowly exchangeable forms are expected to measure (CIESIELSKI and STERCKEMAN 1997; VONA et al., 2020) while with the X-ray fluorescence (XRF) the total content of nutrients is determined (WEINDORF et al., 2014).

3.4.1 Mehlich 3 method

Mehlich (1954) introduced the Mehlich 1 (double acid, M1) procedure for the evaluation of acid sandy soils. This method has been widely used since its introduction, particularly in America and Latin America (MATEJOIC and DURACKOVA 1994; VAN RAIJ 1994; TUCKER et al., 1996). The M1 procedure was updated in 1978 (M2, MEHLICH 1978) to try to extend its use to a wider range of soils. Mehlich 2 (MEHLICH 1978) was the standard extractant for assessing the fertilizer and liming requirements of crops in the Czech Republic/Slovakia up to 1994 (MATEJOVIC and DURACKOVA 1994). Mehlich 3 (M3) (MEHLICH 1984) replaced this procedure in 1981 for two reasons: The chloride in NH_4Cl and HCl was highly corrosive to laboratory instrumentation and (2) EDTA (ethylenediaminetetraacetic acid) was added to Mehlich 3 to enhance the extraction of Mn, Zn and particularly Cu (MEHLICH 1984; TUCKER 1988). Although Mehlich 3 was introduced initially for acid soils its use has been extended to include alkaline soils (TRAN et al., 1990; ALVA 1993; MAMO et al., 1996; SCHMISEK et al., 1998). Mehlich 3 is used in the Czech Republic, Slovakia, and Estonia (FOTYMA and DOBERS 2008).

3.4.2 Cobalt hexamine method

The operating protocol of the cobalt hexamine trichloride (CoHex) method has been described in the study of CIESIELSKI and STERCKEMAN (1997) to determine cation exchange capacity (CEC) and the amount of exchangeable cations. Today the CoHex method is based on the ISO 23470 Standard wherein the exchangeable cations in the sample are replaced by trivalent cobalt hexamine ions. The CEC is calculated from the difference between the initial and final concentrations of cobalt solution which are determined using the analytical method of absorption colorimetry.

3.4.3 Water extraction method

The water extraction method mainly shows the water-soluble forms of each component in the soil. The water extraction method is mostly used for phosphor determination. The water extraction determines P in the soil solution, i.e. dissolved or readily soluble forms of P (WUENSCHER et al., 2015).

3.4.4 XRF method

X-ray fluorescence (XRF) spectrometry nowadays is given much attention as an upcoming proximal soil sensing (PSS) technique. XRF is a quick method for the determination of the total elemental compositions of soil samples (WEINDORF et al., 2014).

3.4.5 Ammonium lactate (AL method)

Ammonium lactate method is also called as **Egnér method** (EGNÉR 1940). This soil test for P is applied in several western European countries, with some countries substituting calcium lactate for ammonium lactate (EGNÉR et al., 1960). In Hungary, the ammonium-lactate acetic acid (AL) extractant is traditionally used in routine soil testing for P, K, Ca and Na analysis.

The AL solution is buffered at an acidic pH (3.75) and extracts P from Al and Fe bound forms by complexation with lactic acid. This acidic solution extracts more phosphorus than the readily available pool because it is also able to dissolve phosphorus (P) reserves (NOVOZAMSKY and HOUBA 1987).

As the availability of the P reserves depends on soil parameters such as $CaCO_3$ content, pH, humus content and soil texture (MENGEL and KIRKBY 2001; BLUME et al., 2016), an AL-P correction model was elaborated for Hungarian soil conditions with converting AL-P values to standard soil properties (plasticity index according to Arany: 37 /loam/; pH/KCl/: 6.8; $CaCO_3$: 0.1%) (THAMM 1980; SARKADI et al., 1987; CSATHÓ 2002).

3.4.6 KCl method

In Hungary, the use of potassium chloride has been standard practice since the 1980s when the national standard for soil testing was created (LOCH 1970). The readily soluble Mg-containing solid constituents and the Mg bound to the soil cation exchange complex are regarded as the plant-available fraction (LOCH 1970). Extraction of the soil, with unbuffered soil solutions like 1M KCl, has been used (MAZAEVA 1967) to extract the plant-available fraction from soils in Hungary. The contents are assessed according to the soil texture. Potassium chloride extracts are also used for the Mg determination in Russia, Belarus, Ukraine and the Balkans.

3.4.7 KCl-EDTA method (ethylenediaminetetraacetic acid)

In Hungary, the Hungarian Standard uses the KCl-EDTA (0.05M EDTA + 0.1 M KCL) extract as a soil test method for the analysis of available micronutrients (MÉM-NAK 1978; BARANYAI et al., 1987; SZŰCS et al., 2003) since 1978. This extract is not used outside of Hungary. Therefore, it is a hard task to compare the results of this method to those of other extractants.

3.5 The studied nutrients

3.5.1 Phosphorus

3.5.1.1 Phosphorus in soil

In soils, P derives mainly from weathering of the primary mineral apatite (SCHLESINGER 1997). The average total P in soils ranges from 200 mg/kg (in older/highly weathered soils) to 800 mg/kg (in younger/less developed soils) (CROSS and SCHLESINGER 1995); **the average amount of organic P ranges between 30% and 65% of the total P** (CONDRON and TIESSEN 2005).

Four major forms of soil P is distinguished in soil:

- P dissolved in soil water,
- P sorbed to surfaces of clay minerals or Fe and Al oxides,

- P in primary phosphate minerals and
- P in organic substances and living organisms.

Accounting for these various P pools, different approaches to extract P from the soil are available and numerous soil P extraction methods have been developed. Several soil properties have been reported to influence the availability of P for plant use and also P extracted by chemical extractants. Such properties include extractable Fe, Al and Mn oxides, clay content of the soil, $CaCO_3$, organic matter, soil pH and P-sorption capacity of the soil (Figure 3) (SHARPLEY 2000).

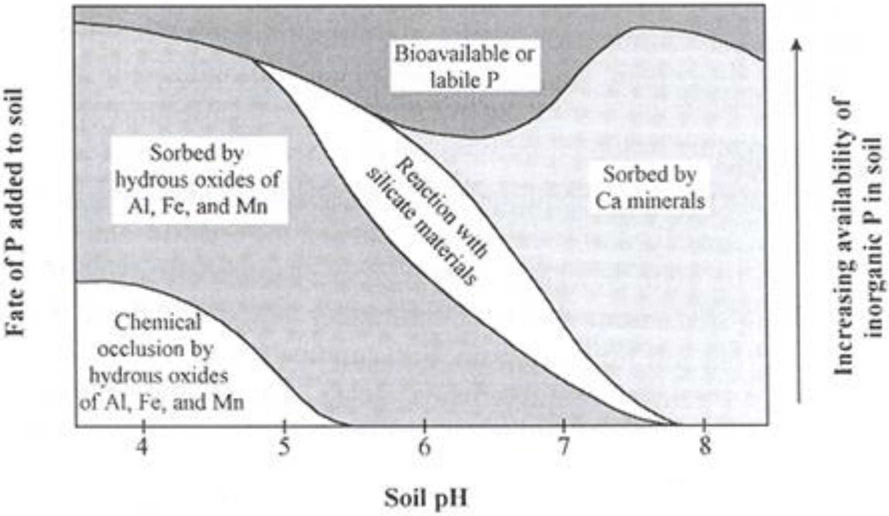


Figure 3: Approximate representation of the fate of P added to soil by sorption and occlusion in organic forms, as a function of soil pH (Source: SHARPLEY 2000)

3.5.1.2 Phosphorus extractants

Phosphorus is one of the most important elements in nutrient management. However, the analysis of phosphorus is one of the most difficult ones. As a result, a great variety of extracting procedures are used (VAN RAIJ 1994: FIXEN AND GROVE 1990). A large number of soil P tests exist, with more than ten different methods available in Europe (Table 2).

Table 2: Methods of soil P analysis in Europe (Tunney et al., 1997)

P test	Method (soil:solution ratio)	Country	Reference
Pw	1:60 (v/v), extraction with water at 20 C, 22h incubation, 1 h shaking	Belgium, the Netherlands, Switzerland	Sissingh,1971
Pw modified	1:50 (v/v), extraction with water at 20 C, 2h shaking	Germany (Hanover)	Schachtschabel and Koster, 1985 (after Sissingh, 1971)
P-AL	1:20 (w/v), 0.1 M ammonium lactate + 0.4 N acetic acid, pH 3.75, 2 h shaking	Belgium, the Netherlands, Hungary	Egner *et al.*, 1955
P-DL	1:50 (w/v), 0.02 M calcium lactate + 0.02M hydrochloric acid, pH 3.7, 1.5 h shaking	Belgium, Germany	Egner and Riehm, 1960
P-CAL	1:20 (w/v), 0.05 M calcium lactate + 0.05 M calcium acetate + 0.3 M acetic acid, pH 4.1, 2 h shaking	Austria, Belgium, Germany	Schuller, 1969
P-NH_4Ac + EDTA	1:5 (w/v), ammonium acetate + EDTA, pH 4.65	Belgium, Switzerland, Finland	van den Hende and Cothenie, 1960
P-EUF	Electroultrafiltration	Austria, Germany	Nemeth, 1979
P Dyer	1:5, citric acid 2%, 4 h shaking	France	Dyer,1894
P Joret-Hebert	1:25, ammonium oxalate 0.2 M, 2 h shaking	France	Joret and Hebert, 1995
P Olsen	20:1 (w/v), 0.5 M sodium bicarbonate, pH 8.5, 1 h shaking	Denmark, France, England, Wales, Northern Ireland, Italy	Olsen *et al.*, 1954
P Morgan	6:30 (v/v), 10% sodium acetate, pH 4.8, 0.5 shaking	Ireland, Scotland	Morgan, 1941

The extractants for P analysis used vary in their strength and mode of operation. Factors such as pH, clay content, organic matter content and amount of free $CaCO_3$ influence the extractability of phosphorus (WUENSCHER et al., 2015). The main criticisms of many of the soil tests are that they fail to give information on the rate of conversion of insoluble P forms to plant-available forms during the growing season (STEVENSON 1986) and do not provide information about the availability of organic forms of P.

The most common extractants for P are, Bray-P1 (BRAY and KURTZ 1945) and M1 on acid and near neutral soils, and Olsen (OLSEN et al., 1954) on calcareous soils (KNUDSEN 1980). Acid ammonium lactate (EGNER et al., 1960) is used in some European countries to extract P and exchangeable cations (VAN RAIJ 1994). Morgan's solution (MORGAN 1941, 1950: PEECH and ENGLISH 1944) is applied to analyse available P in Ireland (BYRNE 1979).

Water is used as an extractant in some laboratories, (VAN RAIJ 1998), and is possibly best from an environmental point of view, (TUNNEY et al., 1998). Some of the newer methods include Mehlich 3, which was developed to replace M1 (MEHLICH 1953) and Bray-P1 (BRAY AND KURTZ 1945) on acid soils. Ammonium bicarbonate-DTPA (Soltanpour and SCHWAB 1977) was designed to replace Olsen (OLSEN et al., 1954) on calcareous soils. Both of these are termed 'universal' extractants because they also extract micronutrients. HOUBA et al., (1990) has proposed 0.01M $CaCl_2$ as an extractant for P and other elements; this method is being evaluated in Europe. Other methods, which are not extraction-based, are described as non-standard (VAN RAIJ 1998). These include electro-ultrafiltration (NEMETH 1982), ion exchange resin (AMER et al., 1955) and iron filter strips (MENON et al., 1988). The extraction of

P with ion exchange resin is the only alternative method that is better than, but it is not as convenient as, the standard soil extractions, (VAN RAIJ 1998).

3.5.2 Magnesium

3.5.2.1 Magnesium in soil

Mg is an essential nutrient element for plant growth and reproduction (MARSCHNER 1995; KOCH et al., 2018). Its deficiency in soils has also been investigated by many authors (YAN and HOU 2018; Li et al., 2019).

Magnesium in soil includes (METSON and BROOKS 1975):

- soluble (Mg-sol),
- readily exchangeable (Mg-rex),
- slowly exchangeable (Mg-sex) and
- structural forms.

Water-soluble Mg forms account for the soil Mg present in the soil solution and in water-soluble precipitates. The readily exchangeable Mg forms, comprise cationic Mg pieces in the diffuse layer, electrostatically adsorbed to negatively charged soil particles (VAN ERP 2002). The slowly exchangeable Mg fraction, includes Mg specifically adsorbed to humic substances (SALMON 1963; MURRAY and LINDER 1984), (hydr)oxides (CHAN et al., 1979) and clay minerals. The structural Mg forms, include the Mg present in the lattices of clay minerals, in carbonates, etc. (BURNS and BURNS 1974; HUNSAKER and PRATT 1970).

Generally, readily exchangeable magnesium accounts for 3–20% of the total soil Mg content (SCHROEDER and ZAHIROLESLAM 1962). However, the concentration of Mg in the soil solution is buffered by the readily available Mg that, in turn, is gradually replenished by the slowly exchangeable Mg and the structural Mg forms (MARSCHNER 1995).

Pot experiments in which soils were depleted, and long-term field experiments of Mg-balance sheet studies have shown that a plant's uptake of Mg is related to the size of the readily exchangeable magnesium (SCHROEDER et al., 1962; RICE and KAMPRATH 1968). Mg is one of the main nutrients in plant nutrition, therefore, in many countries, soils are tested for their Mg content to make sure whether or not it is necessary to apply a Mg fertilizer (RISTIMAKI 2007; ROEMHELD and KIRKBY 2007).

3.5.2.2 Magnesium extractants

Several extractants are used in routine soil testing to determine the soil Mg status, each country has its own validated methods which are best-suited for its soils. Mg soil testing programmes use salt solutions, acidified salt solutions or acid solutions as extractant to assess the "plant-available Mg". The cations or protons added via these extractants replace (part of) the Mg (Mg-rex) resulting in an increased Mg concentration in the solution immediately after the addition (THOMAS 1977). Depending on the extraction time and the affinity of the (specific) adsorption site(s) for Mg and the added cations, the slowly exchangeable Mg (Mgsex) can also be extracted. The acidified extractants may promote the dissolution of the structural forms like Mg containing carbonates and minerals (SPOSITO 1994). The extent of the dissolution strongly depends on procedural aspects like the proton activity, ionic strength, extraction time and soil-solution ratio. When it is assumed that Mg dissolves completely in the extractant (Mg-sol) during the soil extraction, irrespective of the extraction procedure, then the total amount of Mg in the extractant solution (Mg-ext), should equal the sum of the Mg-sol and the changes in the other soil Mg fractions (VAN ERP 2002).

3.5.3 Zinc

3.5.3.1 Zinc in soil

Zinc (Zn) is essential for plant growth, it is taken up as zinc ion (Zn^{2+}). The average Zn concentration in uncontaminated soils is in the range of 17 to 160 µg Zn/g soil (REED and MARTENS 1996). Most of the zinc in soils exists in biologically unavailable forms. According to VIETS (1962), zinc may be present in the soil as:

- water-soluble,
- easily exchangeable,
- adsorbed, precipitated with secondary minerals
- and bound to primary minerals.

The amount of various forms of Zn depends on the soil texture, pH, calcium carbonate-, organic matter content, and other soil characteristics (SHARMA et al., 2004)

The main soil properties controlling the amounts of plant-available forms of Zn in soils include the ‘total’ Zn content, pH and redox conditions, calcite ($CaCO_3$) and organic matter contents, concentrations of all ligands capable of forming organo-Zn complexes, microbial activity in the rhizosphere, concentrations of other trace elements, concentrations of macro-nutrients (especially P) and the soil moisture status (ALLOWAY 2009).

3.5.3.2 Zinc extractants

Soils are tested for zinc in many countries with several extractants. Each country has its validated methods, best-suited for its soils.

As with many other micronutrient cations, the most common, and the most practical approach to analyse Zn is soil is the use of a multinutrient extractant (SIMS and JOHNSON 1991). The most commonly used methods for plant-available Zn include DTPA (LINDSAY and NORVELL 1978), EDTA (VIRO 1955), and 0.1M HCl (PONNAMPERUMA 1981, LIANG and KARAMANOS 1993). The DTPA method of Lindsay and NORVELL (1978) has gained wide acceptance because of good correlations for Zn on calcareous soils, (WHITNEY 1980; JONES and KALRA 1992; WENDT 1995; SCHMISEK et al., 1998).

3.6 The success of the soil analysis starts with representative sampling.

The method of soil sampling and treatment of samples is especially important and it has also an effect on the soil analysis, therefore the way of representative sampling is also introduced in the literature review.

It is essential to take a representative sample for the field if recommendations are to be based on the results of soil tests. The depth of sampling should also remain consistent if soil test results are compared. The time of sampling can also have an effect on recorded soil nutrient levels, for example, P values are usually higher in the winter and early spring, which is believed to be a result of variation in the soil pH and organic matter (COLLINS and BUDDEN 1998).

3.6.1 Representative sample

The ‘success’ of the soil analysis starts with representative sampling. A bulked soil sample needs to **represent the spatial heterogeneity** of the soil in an agricultural field in **both horizontal and vertical directions**. Several soil sampling procedures have been proposed for obtaining a representative soil sample from spatially heterogeneous fields (JAMES and WELLS 1990; LAWRENCE 2020).

Figure 4 visualizes the importance of representative sampling. It is worth recalculating that when a sample is taken from 0-30 cm layer of 5 hectares, it means 18 thousand tons of soil, of which 20 subsamples are homogenized and a total of 1 kg is sent to the laboratory, where most of the soil tests are performed on a few grams of soil. This few grams of soil is presenting the nutrient properties of the 5 hectares (Figure 4).

0-30cm from 5 ha

1 bucket soil is taken from 1 ha

1 kg sample is sent to the laboratory

nutrients are measured decimal accuracy

Figure 4: The ‘success’ of the soil analysis starts with the representative sampling

3.6.2 Horizontal vs Vertical heterogeneity of soils

Soils have horizontal and vertical heterogeneity because of natural variation, e.g., soil-forming processes (Finke et al., 1992), and human influences, e.g., row application of fertilizers (Hofman et al., 1993). Soil sampling protocols should follow this variability in order to obtain representative analytical data and to develop proper soil testing programs (Peck and Soltanpour 1990). To obtain representative samples which accurately reflect the whole field's nutrient status or parts of it, different soil sampling strategies have been proposed (Figure 5) (Kitchen et al., 1990; Mahler 1990; Entz and Chang 1991; Blair and Lefroy 1993; James and Hurst 1995).

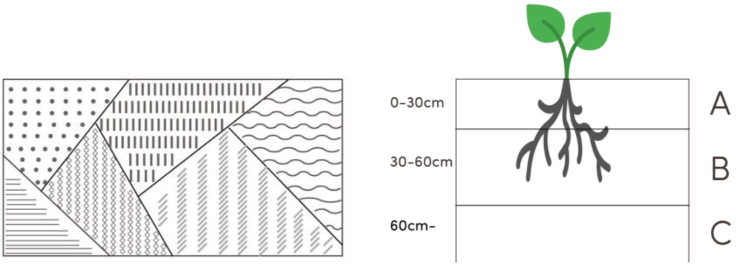


Figure 5: Horizontal and vertical heterogeneity of soils

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

According to Hungarian regulations, soil sampling and analyses are required once in 5 years in 5 ha areas. Rarely, one soil sample per year for the determination of ‘mobile’ nutrient like nitrate is taken. This seems tricky because the soil fertility status may show considerable seasonal variation (Espinoza et al., 1991; Carr and Ritchie 1993). ‘*The sampling frequency of present day soil programs is far from sufficient for strategies that aim at fine-tuning of soil nutrient availability to plant demand. Regular soil analysis during the growing season should become an essential part of these strategies, especially for nutrients which are not well buffered in soils’* (Van Erp 2002).

4. Materials and methods

4.1 Sampling

Seventy geo-referenced soil samples (Figure 6) were taken in Hungary, differing in soil typology, texture, and pH in the summer of 2017. The locations of the 70 samples have been selected according to Minasny-McBratney (MINASNY and MCBRATNEY 2006) and Roudier-Hedley (ROUDIER and HEDLEY 2013). Factors taken into account in this selection were land use, soil type, climate data, accessibility, and market value.

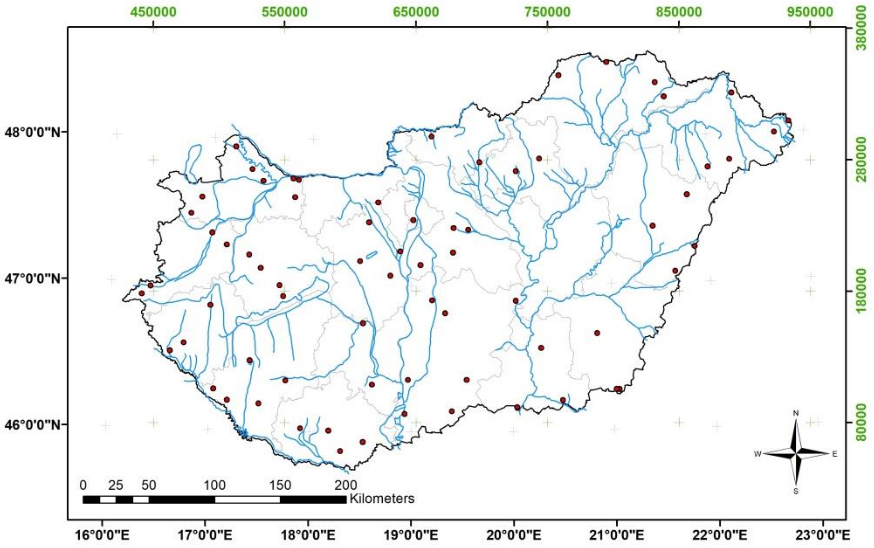


Figure 6: Sampling locations of the soil samples in Hungary

From the 70 samples, 59 pieces were from arable land, 5 from forest, 5 from pasture, and 1 from horticulture area.

Soil samples were taken with an Edelman auger (Figure 7) from the 0-20 cm top layer. The top 2 cm of soil from the sample auger was removed, in order to remove any plant debris that might have fallen into the drill hole.

Figure 7: Soil sampling with Eijkelkamp soil auger

1 kg each of the soil samples were placed into 2 bags. Basic data, such as soil moisture state, land use, land cover, landscape position, slope, and soil erosion data was registered at each sampling location which are presented Annex 1. Samples were transported in a cool box.

4.2 Sample preparation

All the samples were dried within 48 hours from the sample taking moment, at 40ºC, the bigger soil particles were crushed then the samples were sieved through a 2 mm sieve. All remaining stones and visible plant debris and roots remaining in the sieve were thrown away.

One part of the samples were transferred to the Golden Standard Laboratory of Agrocares in Wageningen, the Netherlands. The other part of the samples were sent to the accredited Ökolabor Laboratóriumi Szolgáltató és Kereskedelmi Kft. in Bélmegyer, Hungary.

From each sample, 70 g of soil sample is taken out for particle size analysis at CSFK Laboratory for Sediment and Soil Analysis (SEDILAB) of the Geographical Institute in Budapest, Hungary.

4.3 Laboratory analysis

4.3.1 Studied nutrients

One element from macro-, meso-, and micronutrients was chosen for the data analysis to compare the differences of different analysis methods. Three elements were chosen:

- Phosphorus
- Magnesium
- Zinc

4.3.2 Analysis methods

The selection of international analysis methods was a compromise between agricultural relevance/customer expectations and multi-elemental analysis. The most common analytical procedures (extraction methods and analytical equipment) have been selected to determine the different nutrient pools. A list of possible analytical methods for determining the soil parameters was extracted from a number of ISE (International Soil-analytical Exchange Programme) Quarterly Reports (all reports from 2011) produced by the International Soil-Analytical Exchange (ISE) organized by WEPAL (Wageningen Evaluating Programmes for Analytical Laboratories). This ring test is adopted by soil testing laboratories from all over the world, routine and scientific laboratories. The number of participants varies up to about 80 for the most popular procedures. Supplementary to the results information is given about the procedures and instruments used for the analysis. Together with the results performance was estimated for the different approaches.

As a conclusion of this study the following methods were selected:

- Mehlich 3
- Cobalt hexamine trichloride
- Water extraction
- XRF (X-ray fluorescence)

Mehlich 3 was selected as multielement extraction for the determination of bioavailable pool of nutrients. The Mehlich-3 analysis method is used and accepted worldwide. Furthermore, the accuracy and precision of the method show very low interlaboratory variation compared to different methods.

Cobalt hexamine trichloride was chosen since this method is relatively simple and allows to determine multiple bases and CEC in one procedure without compromising accuracy.

Water extraction was chosen mainly to determine pH and EC and to measure the water-soluble forms of each component in the soil.

The total amount of nutrients are determined with **XRF** due to method convenience such as relatively low cost, low labour, operator and environmentally friendly. Most laboratories use ICP to determine the total pool of nutrients. Sample preparation for ICP requires the usage of strong acids like HF (total) or aqua regia (so-called total) or nitric acid with H_2O_2 (semi total). The procedure is very labour intense, operator and environment unfriendly. The XRF is a compromise between information that can be obtained, cost, environmental impact and accuracy. (These data obtained with classical wet chemistry methods are used to build prediction models for NIR and MIR at Agrocares (www.agrocares.com)).

4.3.2.1 Mehlich 3 method (M3) (Agrocares)

Mehlich 3 method is implemented following Chapter 5 of Recommended Soil Testing Procedures for the Northeastern United States (WOLF et al., 2009). The sample is extracted with Mehlich 3 solution (0.2 mol dm^{-3} acetic acid, 0.015 mol dm^{-3} ammonium fluoride, 0.013 mol dm^{-3} nitric acid, 0.25 mol dm^{-3} ammonium nitrate, 0.001 mol dm^{-3} ethylenediaminetetraacetic acid, pH 2.5), with an application of soil to solvent ratio 1:10 (m V^{-1}), shaken for 5 minutes, then filtered and measured by ICP-MS.

4.3.2.2 Cobalt hexamine trichloride method (CoHex) (Agrocares)

The cobalt hexamine method is implemented following ISO 23470:2007. Cations retained by the soil sample are exchanged with the hexamine cobalt ions of an aqueous solution (0.0166 mol dm^{-3}) after shaking for 60 minutes. The Cation Exchange Capacity CEC is determined by the difference between the initial quantity of hexamine cobalt in solution and the quantity remaining in the extract after the exchange reaction. The quantities of exchanged ions (zinc, magnesium and phosphorus) are determined in the same extract. The measurement of hexamine cobalt concentration in the extract is performed by ICP-MS measurement of the Co concentration which is compared to the concentration of a blank solution.

4.3.2.3 Water extraction method (WA) (Agrocares)

12 grams of air-dried soil is mixed with deionized water in the ratio of 1:5 ($m\ V^{-1}$) After 30 minutes of shaking and filtering the extract is analyzed by ICP-MS.

In case of phosphorus, with the water extraction both P and PO_4 were separately measured. In data analysis, the P-WA(PO_4) measurements were converted to P. Zn and Mg were also measured in water extraction.

4.3.2.4 XRF method (Agrocares)

The procedure is done following ISO 18227:2014 standard. The total element content of soils was determined with an energy dispersive X-ray fluorescence spectrometer (ED-XRF) after milling and pelleting a subsample of 30g to 1mm particle size.

XRF method measures the total amount of phosphorus, magnesium and zinc.

4.3.2.5 AL-method (AL) for phosphate measurements (Ökolabor)

The Phosphorus content analysis of the soil samples in the Hungarian laboratory was implemented according to the standard MSZ 20135:1999. The sample was extracted in the Ammonium lactate (AL) solution (0.1 mol dm^{-3} ammonium lactate, 0.4 mol dm^{-3} acetic acid) with the application of soil to solvent ratio 1:20 ($m\ V^{-1}$), shaken with an overhead shaker for 2 hours, then filtered and analyzed with ICP-AES.

According to the Hungarian standard, AL method is used for the phosphate analysis.

4.3.2.6 KCl method for magnesium measurements (Ökolabor)

The Mg content of the soil samples was analyzed with Potassium chloride (KCl) extract using the traditionally accepted standard (MSZ20135:1999). The samples were extracted in a 1 mol dm^{-3} KCl solution, a soil to solvent ratio of 1:2.5 and stirred for 1 hour, then filtered and analyzed with ICP-AES.

KCl method is applied for magnesium official analysis in Hungary.

4.3.2.7 KCl-EDTA method for zinc measurement (EDTA) (Ökolabor)

KCl-EDTA method is implemented according to the Hungarian standard (MSZ 20135:1999).

The sample was extracted with potassium chloride-EDTA-solution (0.05 mol dm^{-3} EDTA, 0.1 mol dm^{-3} potassium chloride) with the application of soil to solvent ratio 1:2 (m V^{-1}), shaken with an overhead shaker for 2 hours, then filtered and analyzed with ICP-AES.

4.3.2.8 pH (KCl) (Ökolabor)

pH(KCl) was determined with a potentiometric method according to the Hungarian standard (MSZ-08-0206-2:1978). The pH value was measured in a soil suspension, prepared with 1 mol dm^{-3} KCl solution with soil to a solvent ratio of 1:2.5 (m V^{-1}). The suspension was left to stand overnight before measuring.

KCL method is used for Zinc analysis in Hungary.

4.3.2.9 $CaCO_3$-content (Ökolabor)

The $CaCO_3$-content was determined using the gas volumetric method of Scheibler (MSZ-08-0206-2:1978). The carbonates present in the sample were converted into CO_2 by adding HCl-solution to the sample. Carbonate content was calculated from the volume of the generated gas, the temperature, and the air pressure.

4.3.2.10 Arany-type soil texture index (Ökolabor)

The texture index is determined by Liquid limit according to Arany method based on the Hungarian Standard (MSZ-08-0205:1978). This test quantifies the amount of water in cm^3 added (by continuous mixing) to 100 g of an air-dried soil sample to obtain a yarn (upper limit of plasticity), the gained value is the liquid limit according to Arany texture index (STEFANOVITS et al., 1999). The more water the soil absorbs at the upper limit of plasticity, the more clay the soil contains.

4.3.2.11 Clay particle size fraction (SEDILAB)

Particle size distribution was measured using laser diffractometry (Fritsch Analysette 22 Microtech Plus). For breaking down the aggregates, organic matter and $CaCO_3$ content were removed from the samples using H_2O_2 and 10% HCl respectively. For the complete disaggregation, 0.5 mol dm^{-3} sodium-pyrophosphate addition and ultrasonic treatment were applied during the measurement. To calculate the size distribution, the Mie theory was used applying a 1.54 refractive index value.

4.4 Data analyses of the influencing factors

To evaluate the role of soil properties affecting the P, Mg, Zn extraction efficiency samples were grouped according to pH, $CaCO_3$ content, liquid limit according to Arany, and clay content.

4.4.1 Evaluation of the nutrient contents in the view of the influencing factors in the Hungarian advisory system

4.4.1.1 Evaluation of phosphorus in the view of the influencing factors in the Hungarian advisory system

In the Hungarian advisory system, $CaCO_3$ content and soil type (place of production category) is the influencing factor for the assessment of phosphate availability in the soil. This study is concentrating on the soil analysis methodology in the laboratory so just the lime content was taken into consideration in the data analysis.

The evaluation of phosphorus availability is according MÉM-NAK (ANTAL et al., 1979; BUZÁS et al., 1979) if the lime content is smaller or higher than 1 w/w % (Table 3).

Table 3: The effect of $CaCO_3$

$CaCO_3$ w/w %	n
<1 $CaCO_3$	44
>1 $CaCO_3$	26

n=sample size

4.4.1.2 Evaluation of magnesium in the view of the influencing factors in the Hungarian advisory system

In the Hungarian advisory system, the liquid limit according to Arany is considered as an influencing factor of the availability of magnesium in the soil.

The evaluation of the magnesium supply was according to the table (BUZÁS 1983) below Table 4.

Table 4: The evaluation of magnesium supply

Liquid limit according to Arany **(KA)**	Mg mg/kg			
	n	**low**	**moderate**	**good**
<30 sandy soil	0	<40	40-60	60<
30-42 sandy loam, loam soils	58	<60	60-100	100<
>42 clayey loam, clay soil	12	<100	100-200	200<

n=sample size

Besides the liquid limit according to Arany, the importance of lime is also emphasized in the advisory. Magnesium content was evaluated based on the lime categories according to the Hungarian advisory system (Table 5).

Table 5: Limits for the carbonated lime content of the soil

CaCO3 w/w %	**Category**	n
<0.1	lime free	27
0.1-4.9	low lime	30
5.0-19.9	moderate lime	13
>20	high lime	0

n=sample size

4.4.1.3 Evaluation of zinc in the view of the influencing factors in the Hungarian advisory system

The limits of EDTA soluble Zn are classified according to the liquid limit according to Arany. Evaluation of soil EDTA-soluble Zn supply (mg/kg) according to Buzás, 1983 is presented in Table 6.

Table 6: The evaluation of zinc supply

		Zn (mg/kg)	
Liquid limit according to Arany (KA)	n	weak	good
<38 (sand)	29	<1.0	1.0<
38-50 (loam)	40	<2.5	2.5<
>50 (clay)	1	<3.5	3.5<

n=sample size

4.4.2 Grouping of influencing factors in the pairwise analysis

In the further data analysis, the samples were grouped differently from the categories used in Hungary to investigate the more detailed dependence of phosphorus, magnesium, zinc versus pH(KCl), $CaCO_3$, AK, Clay content more accurately.

4.4.2.1 Grouping of the samples based on pH

The samples were grouped differently from the pH categories used in Hungary to investigate the dependence of pH from another perspective.

The used pH categories in Hungary are the followings:

<4.5 – strongly acid
4.5–5.4 - acid
5.5–6.7 – weakly acid
6.8–7.1 – neutral
7.2–7.9 – weakly alkaline
8< – alkaline

In this study the soils were divided into five groups by pH, the more detailed groups followed the sample numbers, all groups have a minimum of 11 samples (Table 7).

Table 7: pH groups with the number of samples analyzed

Groups (n-sample numbers)	pH (KCl)
Group 1 (n = 11)	3.39–4.35
Group 2 (n = 11)	4.36–5.47
Group 3 (n = 12)	5.48–6.78
Group 4 (n = 13)	6.79–7.2
Group 5 (n = 23)	7.21–8.14

4.4.2.2 Grouping of the samples based on $CaCO_3$

Most of the samples tested in our study were in the lime-free or low-lime categories, so samples were grouped differently from the categories used in Hungary to investigate the dependence of phosphorus, magnesium, zinc versus lime content in a more detailed manner. The carbonate content was divided into five groups (Table 8). Sample numbers were the basis for creating the groups, the minimum sample number was seven.

Table 8: $CaCO_3$-groups with the number of samples analyzed and with limits of the formed groups

Groups (n-sample numbers)	**$CaCO_3$-content (w/w %)**
Group 1 (n = 27)	< 0.1
Group 2 (n = 17)	0.11–0.84
Group 3 (n = 7)	0.85–3.16
Group 4 (n = 9)	3.17–8.79
Group 5 (n = 10)	8.80–18.71

4.4.2.3 Grouping of the samples based on Arany-type texture (KA) index

The value ranges for the Arany-type texture coefficient according to the Hungarian advisory system are summarized in Table 9.

Table 9: Liquid limit according to Arany and the corresponding soil texture class

Soil textures	**KA**
Coarse sand	<25
Sand	25–30
Sandy loam	30–37
Loam/silt	37–42
Clayey loam	42–50
Clay	50–60
Heavy clay	60<

For a better understanding of the effect of the Liquid limit according to Arany, the soils were divided into 8 texture groups (Table 10).

Table 10: Liquid limit according to Arany texture groups with the number of samples analyzed

Groups (n-sample numbers)	KA
Group 1 (n = 11)	32–34
Group 2 (n = 10)	35–37
Group 3 (n = 8)	38–38
Group 4 (n = 14)	39–40
Group 5 (n = 10)	41–41
Group 6 (n = 5)	42–42
Group 7 (n = 6)	43–44
Group 8 (n = 6)	45–51

4.4.2.4 Clay particle size fraction grouping

On the triangle for texture identification, the clay content groups are 0–10, 10–20, 20–30 . . . etc. Our smallest figure was 6.8%, and the biggest was 24.89%, so we created the analyzed categories accordingly (Table 11). The clay particles were in the 0–0.002 mm fraction.

(Laser diffraction estimates particle size in 3D (v/v), whereas the pipette method is based on particle deposition. Therefore, the clay limit is not 2u for the results measured with the laser. Initially, it is said that 8u, now it is between 5-6u. That is, the clay content <5u measured with the laser can correspond to the value <2u measured with the pipette.)

Table 11: Clay particle size groups and sample numbers

Groups (n-sample numbers)	Clay particle size (v/v %)
Group 1 (n = 8)	6.82–9.64
Group 2 (n = 24)	9.65–12.74
Group 3 (n = 14)	12.75–15.69
Group 4 (n = 13)	15.70–18.59
Group 5 (n = 6)	18.60–21.82
Group 6 (n = 5)	21.83–24.89

4.4.3 XRF as the measurement method of the total amount of nutrients

The study aims to compare the extraction efficiency of different methods. As the XRF method was applied to determine the total contents and based on its results, it was calculated how much percentages of the total P/Zn/Mg (XRF) could be measured with the different analysis methods. The proportion of the extracted nutrient was calculated from the ‘Total content of nutrients’, XRF measurements.

4.5 Statistical analysis

4.5.1 Descriptive statistics

Soil properties and the analysis methods are described using descriptive statistics with the following statistical indicators: arithmetic mean, median, coefficient of variation (CV), Standard deviation (RSD), maximum (Max), minimum (Min) value.

4.5.2 Linear regression

Linear regression was used to determine the linear relationship between the P, Mg, Zn determination methods, where R^2 presents a percentage of the variability explained by the model. The chosen level of significance was 5%.

4.5.3 Pearson correlation analysis

Pearson correlation analysis was used to determine the relationship between the extraction methods and the soil parameters (pH, $CaCO_3$, KA, Clay).

4.5.4 Normality test

The normality of the data series of the different analysis methods was tested with the Kolmogorov-Smirnov test. If the data of the analysis methods were not normally distributed, then a non-parametric Friedmann ANOVA test was used. If the data of the analysis methods showed normal distribution, then a parametric, Repeated Measures ANOVA test was used.

4.5.5 Wilcoxon signed-rank test

The Wilcoxon signed-rank test, a non-parametric statistical hypothesis test was used to compare the analysis methods (WA, EDTA, M3, CoHex, KCl, Al) to assess whether their mean ranks differed.

4.5.6 Pairwise analyses test

Investigating the pH (KCl), $CaCO_3$-content, liquid limit according to Arany, clay content dependence, pairwise analyses test, a type of location test that is used to compare measurements of the analyses methods to assess whether their means differed.

4.5.7 Box plots

Box plots diagrams were used to display the variation in the phosphorus, magnesium and zinc determination methods.

4.6 Methodology of the data analysis

Three elements are selected for detailed statistical analysis: P, Mg and Zn. The methodology of data analysis was the same for all three elements. The main steps of data analysis are the following:

1. Descriptive statistics of the analysis results
2. Comparison of all methods with linear regression models
3. Calculating percentages of the total P/Zn/Mg (XRF) that could be measured with the different analysis methods
4. Normality test for all data
5. Boxplot analysis of the different measurement methods based on the percentage that each method could measure from the total amount of nutrients (XRF)
6. Pairwise analyses of the different measurement methods based on the percentage that each method could measure from the total amount of nutrients (XRF)
7. Investigating the effect of soil parameters on the different analysis methods based on the percentage that each method could measure from the total amount of nutrients (XRF)
    a. Pearson correlation analysis to get an overview of which soil parameters affects the extracted magnesium of different analysis methods
    b. Evaluation of the measured nutrient contents in the view of the influencing factors in the Hungarian advisory system with linear regression analysis
    c. Evaluating the effect of pH(KCl), $CaCO_3$, liquid limit according to Arany, Clay on the methods with pairwise analysis

5. Results

5.1 General description of the dataset

The descriptive statistics of the 70 soil sample set are presented in Table 12.

Table 12: The basic statistical data of the soils as per pH level, AK, $CaCO_3$, clay contents (n = 70)

Indicators	**pH(KCl)**	**KA**	**$CaCO_3$ w/w %**	**Clay v/v %**
Mean	6.2	39	2.6	14.3
RSD	1.3	3.9	4.2	4.4
Median	7	39	0.4	13.3
CV	0.2	0.1	1.6	0.3
Min	3.4	32	0.1	6.8
Max	8.1	51	18.7	24.9

RSD – standard deviation; CV – coefficient of variation; KA - liquid limit according to Arany

The pH (KCl) of the sample set was between 3.4 and 8.1. The calcium carbonate was diverse in the sample set from 0.1 to 18.7%. The median $CaCO_3$ content was 0.4, which means that many samples were in the lime-free or low-lime category. Nevertheless, there was a sufficient number of samples (min. 7) in each $CaCO_3$ category to evaluate the effect of the higher $CaCO_3$ contents as well. The carbonate content showed the highest variability (CV=1.6). The liquid limit according to Arany was between 32 to 51 with a mean and median value of 39. There were no extreme sandy and clayey soil in the dataset. The minimum clay content was 6.8% whereas the maximum was 24.9. The average clay content of the sample set was 14.3 %.

5.2 Comparison of phosphorus determination methods

5.2.1 Descriptive statistics of the phosphorus analysis results

The descriptive statistics of the phosphorus content of the soil sample set for data comparison are presented in Table 13.

Table 13: The basic statistical data of the soils as P contents determined by the different methods (No. of samples (n) = 70)

Indicators	**P content (mg/kg)**					
	P-WA(PO_4)	**P-WA**	**M3**	**CoHex**	**AL**	**XRF**
Mean	1.8	1.6	56.3	1.9	108.4	597.1
RSD	2.5	2.8	59.7	2.2	143.4	257.0
Median	0.8	0.3	40.4	1.1	67.7	539.3
CV	1.4	1.7	1.1	1.2	1.3	0.4
Min	0.1	0.3	3.3	0.0	4.4	65.5
Max	13.7	13.9	353.4	14.1	785.6	1266.4

RSD – standard deviation; CV – coefficient of variation

The highest P content was measured by XRF analysis which determines the total amount of P in the soil. The other methods measured much less because these extracts dissolve less P and they are applied to represent the plant-available phosphorus content in the soil. Comparing the four other methods, P-WA showed the lowest whereas M3 had the highest measured Mg content in the soil. The mean and median of the Mg content measured by the four methods resulted in the following order:

P-WA < P-WA(PO_4) < CoHex < M3 < AL < XRF

5.2.2 Comparison of the different P analyses methods

5.2.2.1 Comparison of all the values measured by the six different methods

Firstly, a linear regression model with a significance level of 5% was used to determine the linear relationship of the soil P content measured by the P-WA, P-WA(PO_4), M3, CoHex, AL and XRF methods. In table 14, the R^2 presents a percentage of the variability explained by the model. The figures are presented in Annex 1.

Table 14: The linear regression between the P contents measured by P-WA, P-WA(PO_4), M3, CoHex, AL, XRF methods.

Methods	**R^2**	**p**
P-WA(PO_4) vs P-WA	**0.89**	**$p<0.001$**
P-WA(PO_4) vs M3	**0.72**	**$p<0.001$**
P-WA vs M3	**0.67**	**$p<0.001$**
AL vs XRF	0.49	**$p<0.001$**
CoHex vs AL	0.45	**$p<0.001$**
M3 vs CoHex	0.43	**$p<0.001$**
P-WA(PO_4) vs CoHex	0.39	**$p<0.001$**
P-WA vs CoHex	0.39	**$p<0.001$**
CoHex vs XRF	0.33	**$p<0.001$**
M3 vs AL	0.33	**$p<0.001$**
M3 vs XRF	0.2	**$p<0.001$**
P-WA vs AL	0.09	**$p=0.010$**
P-WA(PO_4) vs AL	0.08	**$p=0.020$**
P-WA(PO_4) vs XRF	0.07	**$p=0.033$**
P-WA vs XRF	0.06	**$p=0.036$**

R^2 – the percentage of the variability explained by the model; p – significance level

The linear relationship between P content determined by WA(PO_4) and WA methods is significant, and the determination coefficient is 0.89 (R^2=0.89 $p < 0.001$). 72% of the variance is explained with the significant linear relationship between the P content determined by WA(PO_4) and M3, 67% variance explained with the relationship between P-WA and M3, only 49% of the variance is explained with the relationship between AL and XRF methods, 45% for CoHex vs AL, 43% M3 vs CoHex. The linear relationship for the P content determination method pairs is significant but is explaining less than 40% of the total variation.

5.2.2.2 Comparison of all the values measured by the five different methods

Table 15 shows the different RSD and mean, median, min and max percentages that each method could measure from the total amount of P (XRF).

Table 15: Proportion of measured P from the total amount (XRF)

	% P from the total amount of P, measured with XRF				
Indicators	**P-WA(PO_4)**	**P-WA**	**M3**	**CoHex**	**AL**
Mean	0.31	0.29	9.93	0.30	15.62
SD	0.39	0.44	9.80	0.25	13.49
Median	0.13	0.09	7.15	0.21	11.29
Min	0.01	0.02	0.28	0.00	1.01
Max	1.64	2.46	44.13	1.24	68.67

RSD – standard deviation

The mean percentage values resulting from all the P determination methods showed the following order of measured magnitude:

P-WA < CoHex < P-WA(PO_4) < M3 < AL

The next section is showing the results of the statistical analysis based on all the data. According to the Kolmogorov-Smirnov test, the distribution of the data was not normal. This is why the non-parametric, Friedman's Two-way analysis of variance by ranks (ANOVA) test was used. The results of the statistical analysis were Fr=216.126 df=4, p<0.0001.

The results of the pairwise analyses showed that M3 is not different from AL just as well as P-WA(PO_4), P-WA and CoHex produced similar values but the two groups (M3 and AL versus P-WA(PO_4), P-WA and CoHex) showed significant differences. The boxplot also proved that there are two separate groups (Figure 8).

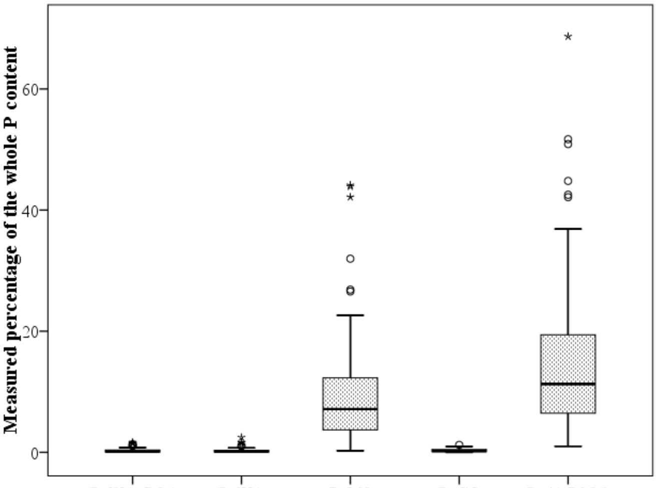


Figure 8: Results of the Boxplot analysis of 5 different P measurement methods based on the percentage that each method could measure from the total amount of P, measured by a sixth method (XRF)

(P-WA(PO_4) = water soluble PO_4, P-WA = water soluble P, M3 = Mehlich 3, CO = Cobalt hexamine, AL= Ammonium lactate

Table 16 shows the significant differences of the five different P-extraction methods.

Table 16: Results of the Pairwise analyses of 5 different P measurement methods based on the percentage that each method could measure from the total amount of P, measured by a sixth method (XRF)

Methods	**significance level**
P-WA vs P-WA(PO_4)	$p = 1$
P-WA vs CoHex	$p = 0.614$
P-WA vs M3	**$p < 0.001$**
P-WA vs AL	**$p < 0.001$**
P-WA(PO_4) vs CoHex	$p = 0.975$
P-WA(PO_4) vs M3	**$p < 0.001$**
P-WA(PO_4) vs AL	**$p < 0.001$**
CoHex vs M3	**$p < 0.001$**
CoHex vs AL	**$p < 0.001$**
M3 vs AL	$p = 1$

There were significant differences between the results of P-WA and P-WA(PO_4) vs M3 and AL results.

The results of CoHex vs M3 and CoHex vs AL methods were also significantly different.

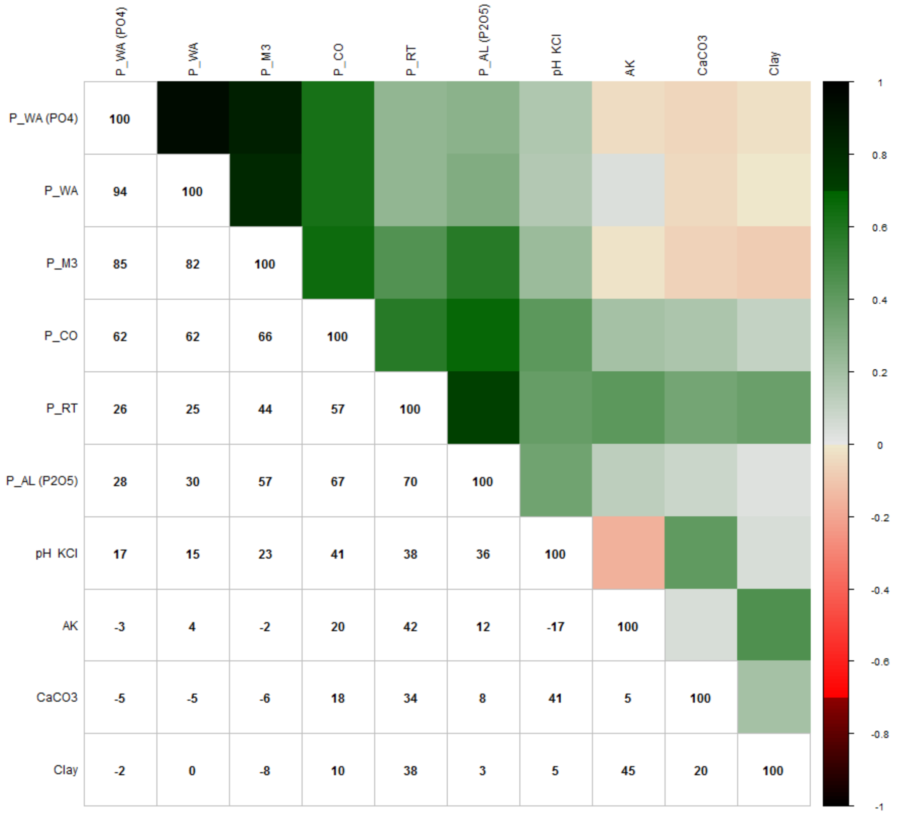
There was no significant difference between P-WA vs P-WA(PO_4), P-WA vs CoHex, P-WA(PO_4) vs CoHex and M3 vs AL.

5.2.3 The effect of soil parameters on the P analyses methods

5.2.3.1 Pearson correlation analysis

Investigating the effect of pH(KCl), $CaCO_3$-content, liquid limit according to Arany and clay content, Pearson correlation analysis, and pairwise analysis tests were applied.

Figure 9 shows the results of the Pearson correlation analysis to get an overview of which soil parameters affect the extracted phosphorus of different analysis methods (P-WA(PO_4) = water-soluble PO_4, P-WA = water-soluble P, M3 = Mehlich 3, CO = Cobalt hexamine, AL= Ammonium lactate, RT = XRF method)



	P_WA (PO4)	P_WA	P_M3	P_CO	P_RT	P_AL (P2O5)	pH KCl	AK	CaCO3	Clay
P_WA (PO4)	100									
P_WA	94	100								
P_M3	85	82	100							
P_CO	62	62	66	100						
P_RT	26	25	44	57	100					
P_AL (P2O5)	28	30	57	67	70	100				
pH KCl	17	15	23	41	38	36	100			
AK	-3	4	-2	20	42	12	-17	100		
CaCO3	-5	-5	-6	18	34	8	41	5	100	
Clay	-2	0	-8	10	38	3	5	45	20	100

Figure 9: Pearson correlation (x*100) analysis between the soil parameters and P analysis methods (red: darker the red weaker the correlation green: darker the green stronger the correlation)

Comparing the P analysis methods, there was a very strong correlation between P-WA and P-WA(PO_4) (r=0.94), M3 and P-WA(PO_4) (r=0.85), M3 and P-WA (r=0.82). A strong correlation was found between CoHex vs P-WA(PO_4) and P-WA (r=0.62) methods, CoHex vs M3 method (r=0.66), AL vs CoHex (r=0.67) and AL vs XRF (r=0.70) methods. There was a moderate correlation between XRF vs M3 (r=0.44), XRF vs CoHex (r=0.57) and AL vs M3 (r=0.57) methods.

According to the correlation analysis, the effect of soil parameters on the extracted phosphorus was moderate or weak. pH(KCl) showed moderate correlation with analysis results of CoHex method (r=0.41) and weak with M3 (r=0.23), XRF (r=0.38) and AL (r=0.36) methods. KA showed a moderate correlation with the results of XRF (r=0.42) and a weak correlation with the measurements of CoHex (r=0.20) method. $CaCO_3$ (r=0.34) content and Clay (r=0.38) content showed a weak correlation only with the results of XRF method.

5.2.3.2 Evaluation of the measured P contents in the view of the influencing factors in the Hungarian advisory system

In the Hungarian advisory system, $CaCO_3$ content is considered as the influencing factor for the availability of phosphate in the soil.

Table 17 shows the different percentages that each method could measure from the total amount of P (XRF) in the case of the two $CaCO_3$ groups.

Table 17: Proportion of measured P from the total amount (XRF) in case of < 1 $CaCO_3$ w/w % and >1$CaCO_3$ w/w % content.

Indicators		% from the total amount of P (XRF)				
	$CaCO_3$ w/w %	**P-WA(PO_4)**	**P-WA**	**M3**	**CoHex**	**AL**
Mean	<1	0.34	0.33	10.80	0.25	12.79
	>1	0.26	0.22	8.47	0.39	20.41
RSD	<1	0.41	0.48	10.57	0.24	10.17
	>1	0.36	0.38	8.32	0.26	16.91
Median	<1	0.16	0.11	7.01	0.16	10.79
	>1	0.13	0.06	7.15	0.42	15.02
Min	<1	0.02	0.03	1.31	0.00	1.09
	>1	0.01	0.02	0.28	0.05	1.01
Max	<1	1.51	2.46	44.13	0.96	51.70
	>1	1.64	1.65	42.15	1.24	68.67

The mean, median, min and max percentage values resulting from the P determination methods showed the different order in the two $CaCO_3$ groups (Figures 10 and 11).

The measured magnitude based on the mean in case of <**1 $CaCO_3$%**:

CoHex < P-WA < P-WA(PO_4) < M3 < AL

The measured magnitude based on the median in case of <**1 $CaCO_3$%**:

P-WA < CoHex ≤ P-WA(PO_4) < M3 < AL

The measured magnitude based on the mean and median in case of >**1 $CaCO_3$%:**

P-WA < P-WA(PO_4) < CoHex < M3 < AL

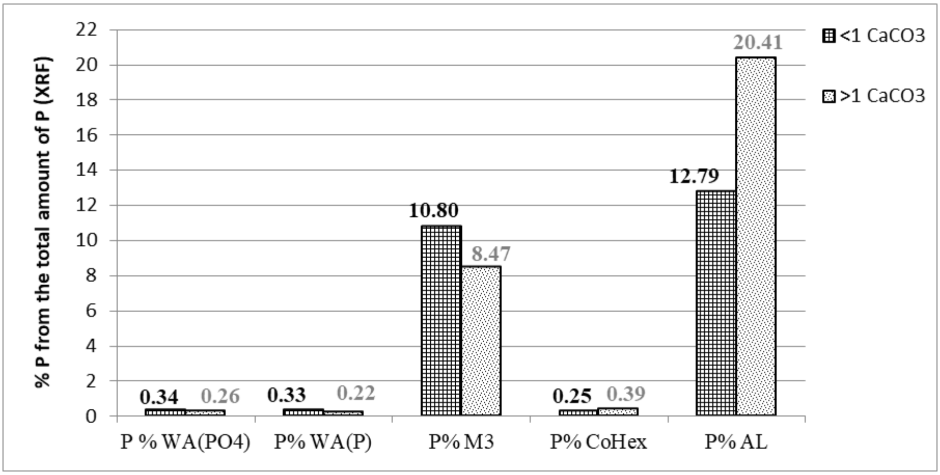


Figure 10: The mean of the measured P % measured by the different amount from the total P (XRF) in case of <1 $CaCO_3$ w/w % and >1 $CaCO_3$ w/w % content.

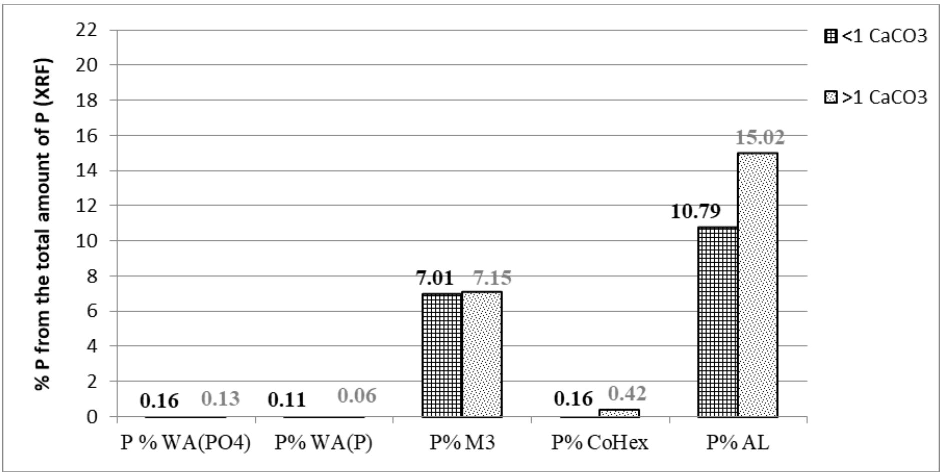


Figure 11: The median of the measured P % measured by the different amount from the total P (XRF) in case of <1 $CaCO_3$ w/w % and >1 $CaCO_3$ w/w % content.

At higher than 1% $CaCO_3$ content, the measured phosphorus from the total was lower in the case of P-WA, P-WA(PO_4) methods.

In case of M3, the results of the median were similar at both $CaCO_3$ levels, but the results of the mean showed higher phosphorus in case of <1 $CaCO_3$ %.

Higher than 1% lime content resulted in higher phosphorus levels in the case of CoHex and AL methods. At higher than 1% $CaCO_3$ content the result of the mean phosphorus was 7.5% higher compared to the soils with <1 $CaCO_3$ %.

At <1 $CaCO_3$ %.the mean of the measured phosphorus with AL method was 12,79 % from the total amount while at >1 $CaCO_3$ % the mean of the measured phosphorus was 20.41%. At higher lime content the measured phosphorus was 37% higher compared to the lower lime content soils.

The higher the calcium, the higher the amount of fixed phosphates, so it means that the AL method extracts more phosphates.

Linear regression with a significance level of 5% was used to determine the relationships of the soil P content measured by the P-WA, P-WA(PO_4) M3, CoHex and AL methods, according to the lime content (Table 18).

Table 18: The linear regression between the measured P percentages (from the total amount XRF) of the different analysis methods in the two lime content categories

	<1 $CaCO_3$ w/w %		> 1 $CaCO_3$ w/w %	
Methods	**R^2**	**p**	**R^2**	**p**
P-WA(PO_4) vs P-WA	**0.66**	**$p<0.001$**	**0.93**	**$p < 0.001$**
P-WA(PO_4) vs CoHex	0.28	**$p<0.001$**	0.40	**$p=0.001$**
P-WA(PO_4) vs **AL**	0.41	**$p<0.001$**	0.00	$p=0.889$
P-WA(PO_4) vs M3	**0.76**	**$p<0.001$**	**0.72**	**$p<0.001$**
P-WA vs CoHex	0.43	**$p<0.001$**	0.36	**$p=0.001$**
P-WA vs **AL**	0.57	**$p<0.001$**	0.00	$p=0.770$
P-WA vs M3	0.57	**$p<0.001$**	**0.74**	**$p<0.001$**
CoHex vs **AL**	0.39	**$p<0.001$**	0.20	**$p=0.022$**
CoHex vs M3	0.28	**$p<0.001$**	0.28	**$p=0.006$**
AL vs M3	0.40	**$p<0.001$**	0.10	$p=0.117$

R^2 – the percentage of the variability explained by the model; p – significance level

Comparing the AL method that is applied in the Hungarian advisory system with the other methods showed that in lime-free, low $CaCO_3$ content soils the linear relationship between P-WA(PO_4) and M3 methods had the highest determination coefficient (R2=0.756) explaining 75.6% of the variance. In this soil category, each method pair shows a significant linear relationship, P-WA(PO_4) vs P-WA explaining 66.3% variance, P-WA vs AL 56.7%, P-WA vs M3 56.5%, P-WA vs CoHex explaining 43.3% variance, P-WA(PO_4) vs AL explaining 40.6%. All the other pairs have lower determination coefficients.

For the soil category with >1 $CaCO_3$% content, the linear relationship between P-WA(PO_4) and P-WA methods is significant and explains 92.7% variance showing a strong relationship. A significant relationship between P-WA vs M3 explains 74.3% variance and 72.3% for P-WA(PO_4) vs M3. The relationship between P-WA(PO_4) vs AL, P-WA vs AL and AL vs M3 is not significant while all other significant pairs showed determination coefficients lower than 0.4 – explaining less than 40% of the total variance.

5.2.3.3 Evaluating the effect of soil parameters with pairwise analysis

Further investigating the effect of soil parameters, pairwise analysis tests and a type of location test were used to compare measurements of the five phosphorus analysis methods to assess whether their means differed. The proportions of measured P from the total amount (XRF) were used in the comparison and they were classified according to specified pH, $CaCO_3$ content, liquid limit according to Arany, and clay content groups.

Comparison of the measured values in the pH groups

The pairwise analyses of the measured phosphorous percentages compared with the measured total phosphorous amounts based on the pH groups showed differences between the methods.

Based on the data evaluation of the analysis methods, a non-normal distribution was found in Group 1, 2, 4, 5 so a non-parametric Friedmann ANOVA test was used. In Group 3 the data of the analysis methods showed normal distribution, as a result, a parametric Repeated Measures ANOVA test was used.

Group 1-2-3: In the first two pH groups (pH 3.39–4.35, 4.36–5.47 and 5.48–6.78) the results of P-WA vs CoHex and M3 vs AL methods were not significantly different in these acid groups. The two P-WA phosphorus measurements and AL, M3 methods were significantly different from each other. CoHex method measured a significantly different amount of P compared to M3 and AL (Table 19).

Group 4: In the fourth group **(**pH 6.79–7.2) P-WA vs CoHex and M3 vs AL methods were not significantly different like in groups 1, 2, 3. The results of P-WA and Cohex methods were not significantly different but the CoHex method here was no longer significantly different from M3, only from AL (Table 19).

Group 5: Based on the comparison between the groups, in the fifth pH group (pH 7.21–8.14) M3 was not different from AL method. CoHex and M3 were also not significantly different, while CoHex was significantly different from AL methods. The results of the two P-WA methods were similar, but in this group, P-WA was significantly different from CoHex, while P-WA(PO_4) was not significantly different from CoHex (Table 19).

Table 19: Pairwise analysis of the measured phosphorous percentages compared with the measured total phosphorous amounts based on the pH(KCl) groups

	Group 1	**Group 2**	**Group 3***	**Group 4**	**Group 5**
pH(KCl)	3.39-4.35	4.36-5.47	5.48-6.78	6.79-7.20	7.21-8.14
P-WA(PO_4) vs P-WA	$p=1$	$p=1$	$p=1$	$p=1$	$p=1$
P-WA(PO_4) vs CoHex	$p=1$	$p=1$	$p=1$	$p=0.825$	**$p<0.015$**
P-WA(PO_4) vs AL	**$p<0.001$**	**$p<0.002$**	**$p<0.001$**	**$p<0.001$**	**$p<0.001$**
P-WA(PO_4) vs M3	**$p<0.001$**	**$p<0.001$**	**$p<0.001$**	**$p<0.001$**	**$p<0.001$**
P-WA vs CoHex	$p=1$	$p=1$	$p=1$	$p=1$	$p=0.32$
P-WA vs AL	**$p<0.019$**	**$p<0.007$**	**$p<0.001$**	**$p<0.003$**	**$p<0.001$**
P-WA vs M3	**$p<0.002$**	**$p<0.002$**	**$p<0.001$**	**$p<0.001$**	**$p<0.001$**
CoHex vs AL	**$p<0.019$**	**$p<0.007$**	**$p<0.001$**	$p=0.184$	$p=0.068$
CoHex vs M3	**$p<0.002$**	**$p<0.002$**	**$p<0.001$**	**$p<0.002$**	**$p<0.001$**
AL vs M3	$p=1$	$p=1$	$p=1$	$p=1$	$p=0.764$

***Group 3:** Tukey post hoc test

P-WA, P-WA(PO_4) vs AL, M3 methods were significantly different in all pH groups which is understandable since the P-WA is a weak solvent compared to AL and M3 methods that are weak acids.

In group 5, from the two P-WA methods, just the results of P-WA(PO_4) were significantly different from CoHex.

CoHex and M3 methods were significantly different in all pH groups. CoHex and AL methods were significantly different in the first three acid groups but from pH 6.79 the two methods were not different.

There was no significant difference between the results of AL vs M3 and P-WA vs CoHex methods. AL method was significantly different from Cohex, P-WA methods in each pH category.

Comparison of the measured values based on the $CaCO_3$-content groups

Group 1–2: In the first two $CaCO_3$ groups (0–0.84%) P-WA, P-WA(PO_4) vs CoHex and M3 vs AL methods were not significantly different. P-WA, P-WA(PO_4) vs AL, M3 methods were significantly different. CoHex method was also significantly different from AL and M3 methods (Table 20).

Group 3–4–5: In these 3 groups the results were the same as in the first groups except for P-WA(PO_4) vs AL methods. These were not different in these groups (Table 20).

Table 20: Pairwise analysis of the measured phosphorous percentages compared with the measured total phosphorous amounts based on the $CaCO_3$ groups

	Group 1	**Group 2**	**Group 3**	**Group 4**	**Group 5**
$CaCO_3$ w/w %	<0.1	0.11–0.84	0.85–3.16	3.17–8.79	8.80–18.71
P-WA(PO_4) vs P-WA	p=1	p=1	p=1	0.66	p=1
P-WA(PO_4) vs CoHex	p=1	p=1	p=1	0.162	p=1
P-WA(PO_4) vs AL	**p<0.001**	**p<0.005**	p=0.398	p=1	p=0.82
P-WA(PO_4) vs M3	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**
P-WAP vs CoHex	p=1	p=1	p=1	p=1	p=1
P-WA vs AL	**p<0.001**	**p<0.001**	**p<0.016**	**p<0.011**	**0.016**
P-WA vs M3	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**
CoHex vs AL	**p<0.001**	**p<0.001**	**p<0.009**	**p<0.001**	**p<0.016**
CoHex vs M3	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**
AL vs M3	p=1	p=1	p=1	p=1	p=1

The detailed classification based on $CaCO_3$ content showed almost the same results when the pairwise analysis was based on all the data.

The most similar methods were AL vs M3 methods and P-WA(PO_4), P-WA vs CoHex methods.

CoHex vs M3 and AL methods were significantly different in all $CaCO_3$ groups.

In this pairwise comparison, there was **not any significant difference between the results of AL and M3** in the lime groups.

Comparison of the measured values based on the liquid limit according to Arany groups

Group 1–5: In the first five liquid limit according to Arany groups, from sandy loam to loam texture (KA=32–41) P-WA, P-WA(PO_4) methods were significantly different from AL, M3 methods. There was a significant difference between CoHex and AL, M3 methods. The results of CoHex vs P-WA, P-WA(PO_4) and AL vs M3 methods did not show a significant difference (Table 21).

Group 6: In the sixth group (KA=42) just P-WA and P-WA(PO_4) were significantly different from AL. CoHex was significantly different from AL. The differences between the other methods were not significant (Table 21).

Group 7: In the seventh group (KA=43–44) three pairs were significantly different from each other: P-WA vs AL, P-WA(PO_4) vs AL, CoHex vs AL. The differences between the other methods were not significant (Table 21).

Group 8: In the eighth group (KA=45–51) P-WA(PO_4) differed significantly from M3 and Al methods, while P-WA differed only from AL. There was no significant difference between the other methods (Table 21).

Table 21: Pairwise analysis of the measured phosphorous percentages compared with the measured total phosphorous amounts based on the liquid limit according to Arany groups

	Group 1	**Group 2**	**Group 3**	**Group 4**
KA	32-34	35-37	38-38	39-40
P-WA(PO$_4$) vs P-WA	$p=1$	$p=1$	$p=1$	$p=1$
P-WA(PO$_4$) vs CoHex	$p=1$	$p=1$	$p=1$	$p=1$
P-WA(PO$_4$) vs AL	**$p<0.019$**	**$p<0.001$**	**$p<0.009$**	**$p<0.001$**
P-WA(PO$_4$) vs M3	**$p<0.005$**	**$p<0.011$**	**$p<0.027$**	**$p<0.002$**
P-WA vs CoHex	$p=1$	$p=1$	$p=1$	$p=1$
P-WA vs AL	**$p<0.001$**	**$p<0.001$**	**$p<0.003$**	**$p<0.001$**
P-WA vs M3	**$p<0.001$**	**$p<0.007$**	**$p<0.009$**	**$p<0.001$**
CoHex vs AL	**$p<0.007$**	**$p<0.002$**	**$p<0.027$**	**$p<0.001$**
CoHex vs M3	**$p<0.002$**	**$p<0.019$**	$p<0.072$	**$p<0.013$**
AL vs M3	$p=1$	$p=1$	$p=1$	$p=1$

	Group 5	**Group 6**	***Group 7**	**Group 8**
KA	41-41	42-42	43-44	45-51
P-WA(PO$_4$) vs P-WA	$p=1$	$p=1$	$p=1$	$p=1$
P-WA(PO$_4$) vs CoHex	$p=1$	$p=1$	$p=1$	$p=0.679$
P-WA(PO$_4$) vs AL	**$p<0.001$**	**$p<0.014$**	**$p<0.01$**	**$p<0.001$**
P-WA(PO$_4$) vs M3	**$p<0.002$**	$p=0.278$	$p=1$	**$p<0.019$**
P-WA vs CoHex	$p=1$	$p=1$	$p=1$	$p=1$
P-WA vs AL	**$p<0.001$**	**$p<0.014$**	**$p<0.01$**	$p=0.062$
P-WAvs M3	**$p<0.019$**	$p=0.278$	$p=1$	**$p<0.005$**
CoHex vs AL	**$p<0.007$**	$p=1$	**$p<0.01$**	$p=0.446$
CoHex vs M3	**$p=0.109$**	$p=0.093$	$p=1$	$p=1$
AL vs M3	$p=1$	$p=1$	**$p<0.001$**	$p=1$

*Group 7: Tukey post hoc test

In the first 5 liquid limit according to Arany groups, the results of the pairwise analysis were the same.

According to the Hungarian classification of liquid limit according to Arany, group 3-6 belongs to one category which is the loam. The null hypothesis was that in these groups there are similar results of the pairwise analysis but in group 5 the significant differences were less compared to group 3-4-5.

WA vs AL, M3 methods showed the biggest differences, these were significantly different in almost all KA groups.

In all Arany-type categories, there was no significant difference between the following pairs: P-WA(PO_4) vs P-WA, P-WA(PO_4) vs CoHex AL vs M3 and P-WA vs CoHex.

M3 and AL methods were not significantly different except for the 43-44 liquid limit according to Arany category.

Comparison of the measured values based on the clay-content groups

Group 1-5: In the first 5 groups (6.82-21.82%) the results of the pairwise analysis were the same in all groups (except for one result in group four CoHex vs M3 pair was not significantly different while in other groups well). There was no significant difference between P-WA, P-WA(PO_4) vs Cohex and AL vs M3 (Table 22).

Group 6: In the sixth clay group (21.83–24.89) the following pairs were significantly different: P-WA(PO_4), P-WA vs Al and CoHex vs AL (Table 22).

Table 22: Pairwise analysis of the measured phosphorus percentages compared with the measured total phosphorous amounts based on the clay groups

	Group 1*	**Group 2**	**Group 3**
Clay v/v %	6.82–9.64	9.65–12.74	12.75–15.69
P-WA(PO_4) vs P-WA	p=1	p=1	p=1
P-WA(PO_4) vs CoHex	p=1	p=1	p=1
P-WA(PO_4) vs AL	**p<0.001**	**p<0.001**	**p<0.001**
P-WA(PO_4) vs M3	**p<0.01**	**p<0.001**	**p<0.001**
P-WA vs CoHex	p=1	p=1	p=1
P-WA vs AL	**p<0.001**	**p<0.001**	**p<0.001**
P-WA vs M3	**p<0.01**	**p<0.001**	**p<0.002**
CoHex vs AL	**p<0.001**	**p<0.001**	**p<0.001**
CoHex vs M3	**p<0.01**	**p<0.001**	**p<0.019**
AL vs M3	p=1	p=1	p=1

	Group 4	**Group 5***	**Group 6***
Clay v/v %	15.70–18.59	18.60–21.82	21.83–24.89
P-WA(PO_4) vs P-WA	p=1	p=1	p=1
P-WA(PO_4) vs CoHex	p=0.092	p=1	p=1
P-WA(PO_4) vs AL	**p<0.001**	**p<0.001**	**p<0.01**
P-WA(PO_4) vs M3	**p<0.001**	**p<0.01**	p=1
P-WA vs CoHex	p=1	p=1	p=1
P-WA vs AL	**p<0.001**	**p<0.001**	**p<0.01**
P-WA vs M3	**p<0.003**	**p<0.01**	p=1
CoHex vs AL	**p=0.013**	**p<0.001**	**p<0.01**
CoHex vs M3	p<0.35	**p<0.01**	p=1
AL vs M3	p=1	p=1	p=1

***Group 1, 5, 6:** Tukey post hoc test

The results of the pairwise analysis in the different clay groups were almost the same. The classification based on clay showed similar results to the pairwise analysis of all data.

Conclusion based on pH and clay content: the analyses of the pH (KCl) showed that the P-WA(PO_4) was different from the CoHex method.

All-inclusive evaluation of the effect of soil parameters on phosphorus measurements

Summarizing the effect of the soil parameters, it was calculated that how many percentages of the results of the pairwise analysis were significant along with the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay) (Table 23). For example, 20 percent of the pH results from the pairwise analysis were significant.

It helped to evaluate the methods and establish general trends and tendencies.

Table 23: the average of the number of significant results of all the pairwise analysis of the P% measurements along with the four influencing factors (pH(KCl), $CaCO_3$, Arany-type texture, and clay).

	% of the significant results					
Methods	pH	CaCO3	KA%	Clay	Average	**ORDER**
P-WA(PO_4) vs P-WA	0	0	0	0	**0**	**1**
P-WA vs CoHex	0	0	0	0	**0**	**1**
P-WA(PO_4) vs CoHex	20	0	0	0	**20**	**2**
AL vs M3	0	0	87.5	0	**21.9**	**3**
CoHex vs M3	100	100	62.5	67	**82.3**	**4**
CoHex vs AL	60	100	75	100	**83.8**	**5**
P-WA(PO_4) vs AL	100	40	100	100	**85**	**6**
P-WA(PO_4) vs M3	100	100	75	83	**89.6**	**7**
P-WA vs M3	100	100	75	83	**89.6**	**7**
P-WA vs AL	100	100	87.5	100	**96.9**	**8**

av: the average of the significant results
Order: evaluation from 1 to 8 (1: smallest different 8: biggest difference based on all parameters (pH+CaCO3+KA+Clay)

Evaluating the differences based on the four influencing factors resulted in the following order (1 - smallest difference 8 - biggest difference):

1. **P-WA(PO_4) vs P-WA, P-WA vs CoHex**
2. **P-WA(PO_4) vs CoHex**
3. **AL vs M3**
4. **CoHex vs M3**
5. **CoHex vs AL**
6. **P-WA(PO_4) vs AL**
7. **P-WA(PO_4) vs M3, P-WA vs M3**
8. **P-WA vs AL**

P-WA(PO_4) vs P-WA and P-WA vs CoHex were not significantly different from each other. The highest significant difference was between P-WA vs AL method.

5.2.1 Discussions concerning phosphorous measurements

BLOMBÄCK et al. (2021) used pH, clay and total carbon as explanatory variable for regression models aiming at describing phosphorous saturation in the soil but they did not find notable improvements to regression models. It was found that pH and clay do have an influence on the measured, plant-available P content of the soil, so it might as well have an influence on regression models in case model users are aware of the differences in the groups of clay content and pH.

Anion exchange resin method was found to be the highest values for the determination coefficients for the correlations between phosphorous uptake by plants and soil phosphorous content (SILVA and RAIJ,1996). They also found that the resin method shows properly the effect of liming on the increase of P availability in the soil while Mehlich method does not which means Mehlich method underestimates the plant-available phosphorous in the soil. Among the methods analyzed it was found that Mehlich was one of the two methods that measured the highest proportions of the total which is opposite that SILVA and RAIJ 1996 published.

The water-soluble method was not only used but found appropriate for plant-available P-content of the soils of the Netherland as early as the 1960s (NEYROUD and LISCHER 2003). Water-soluble P (PW) measurement was found to be independent of organic matter content, pH, particle size distribution, $CaCO_3$-content but found to be sensitive to Fe_2O_3 content (above 10%). The final conclusion was that PW value is an appropriate value for plant-available P content of the soil, and it is true for a wide variety of soils. It is against the findings of NEYROUD and LISCHER (2003) who found that PW values may underestimate the plant-available phosphorous in the soil. We also found that water-soluble P and PO_4 were similar (and both were similar to the CoHex method) but they all had significant differences against all other methods in all groups of the influencing soil parameters.

In case of the AL method NEYROUD and LISCHER (2003) found that even the five laboratories that they compared have had different values, correlation coefficient (r) was between 0.48 to 0.97 with a standard deviation ranging from 0.25 to 0.54. So, it is difficult to judge the comparisons in case different laboratories provide data with that high differences. However, in our case there was only one laboratory for AL so this problem of measurements with high uncertainty of the multiple laboratories do not apply to our data. And it was out of scope for us to compare other laboratories from other countries.

5.2.2 Conclusions concerning phosphorous measurements

Comparing the different percentages of the measured phosphorous that each method could measure from the total amount of phosphorus (XRF), **ammonium lactate solution proved to extract the highest amount of phosphorus.**

Phosphorus content measured by the six methods resulted in the following order: **P-WA< CoHex < P-WA(PO_4) < M3 < AL < XRF**

The linear relationship between P content determined by P-WA and M3 methods was significant with the determination coefficients of 0.72 for P-WA(PO_4) vs M3 and 0.67 for P-WA vs M3.

The results of the pairwise analyses of the 5 different P measurement methods based on the percentage that each method could measure from the total amount of P (XRF) showed that **M3 is not different from AL just as well as P-WA(PO_4), P-WA and CoHex produced similar values but the two groups (M3 and AL versus P-WA(PO_4), P-WA and CoHex) showed significant differences.**
The boxplot analysis of the 5 different phosphorus analysis methods proved that there are two separate groups (M3, AL versus CoHex, P-WA, P-WA(PO_4).

Evaluating the phosphorus contents according to two lime categories based on the Hungarian advisory system showed that **higher than 1%**

$CaCO_3$ content resulted in much higher phosphorus levels in the case of AL method compared to soils with lower than 1% lime content. The higher the lime content, the higher the amount of fixed phosphates, so it means that AL method extracts not only the available but even the fixed phosphates.

Comparing the results of the AL-phosphorus method (used in Hungary) with the results of P-WA(PO_4), P-WA , CoHex and M3 methods in lime free – low $CaCO_3$ content soils, showed weak significant linear relationships explained at 39%-0,57% ($0.39 \leq R^2 \leq 0.57$) variance. In the category of higher lime content soils, the only significant relationship was determined between CoHex vs AL (p=0.02) explaining 20% of the variance. All the others were not significant ($R^2 < 0.2$; $p \geq 0.05$)

The pairwise analyses of the measured phosphorous percentages of the total phosphorous amounts based on the separate analyses of pH, $CaCO_3$, KA and Clay groups showed smaller differences between the methods, but the results were comparable with the pairwise analysis when all data was included. Based on the average of the number of significant results along with the four influencing factors, the highest significant difference was between P-WA and AL methods. **P-WA(PO_4) vs P-WA and P-WA vs CoHex were not significantly different from each other.**

Evaluating the differences based on all parameters the following order can be made (1: smallest difference 8: biggest difference):

1. **P-WA(PO_4) vs P-WA, P-WA vs CoHex**
2. **P-WA(PO_4) vs CoHex**
3. **AL vs M3**
4. **CoHex vs AL**
5. **CoHex vs M3**
6. **P-WA(PO_4) vs AL**
7. **P-WA(PO_4) vs M3, P-WA(PO_4) vs M3**
8. **P-WA vs AL**

Evaluating the differences based on all parameters it can be concluded that P-WA(PO_4) vs P-WA and P-WA vs CoHex were not significantly different from each other. The highest significant difference was between P-WA vs AL method.

5.3 Comparison of magnesium determination methods

5.3.1 Descriptive statistics of the Mg analysis results

The descriptive statistics of the soil sample set are presented in Table 24.

Table 24: The basic statistical data of the soils as Mg contents determined by the different methods (No. of samples (n) = 70)

Indicators	**Mg content (mg/kg)**				
	WA	**M3**	**CoHex**	**KCl**	**XRF**
Mean	11.1	392.5	356.6	266.7	6210.6
RSD	7.2	284.6	284.3	203.2	3963.1
Median	10.2	325.3	276.1	210.0	6001.2
CV	0.6	0.7	0.8	0.8	0.6
Min	1.9	10.5	7.5	13.0	482.5
Max	51.6	1295.1	1213.1	860.0	21592.3

RSD – standard deviation; CV – coefficient of variation

The highest Mg content was measured by XRF analysis which determines the total amount of Mg in the soil. The other methods measured much less because these extracts dissolve less Mg and they are applied to represent the available magnesium content in the soil. Comparing the four other methods, WA showed the lowest whereas M3 the highest Mg content in the soil. The mean and median of the Mg content measured by the four methods resulted in the following order:

WA < KCl < CoHex < M3 < XRF

5.3.2 Comparison of the different Mg analyses methods

5.3.2.1 Comparison of all the values measured by the five different methods

Firstly, a linear regression with a significance level of 5% was used to determine the relationships of the soil Mg content measured by the Water, Mehlich 3, CoHex, EDTA and XRF methods, as it can be seen in Table 25. The figures of the linear regression analysis are presented in Annex 2.

Table 25: The linear regression with a significance level of 5% between the Mg contents measured by WA, M3, CoHex, KCl, XRF methods

Methods	**R^2**	**p**
KCl vs CoHex	**0.96**	**$p<0.001$**
WA vs M3	**0.68**	**$p<0.001$**
M3 vs CoHex	**0.66**	**$p<0.001$**
M3 vs KCl	**0.60**	**$p<0.001$**
WA vs CoHex	0.32	**$p<0.001$**
M3 vs XRF	0.28	**$p<0.001$**
WA vs KCl	0.25	**$p<0.001$**
WA vs XRF	0.12	**$p=0.003$**
CoHex vs XRF	0.09	**$p=0.013$**
KCl vs XRF	0.06	**$p=0.034$**

R^2 – the percentage of the variability explained by the model; p – significance level

The linear regressions between all the pairs of Mg content measurement methods are significant, but only 4 of them explain more than 60% of the total variation. The linear relationship between KCl and CoHex methods has the highest determination coefficient (R^2=0.96), followed by WA – M3 (R^2=0.68), M3 – CoHex (R^2=0.66) and M3 – KCl (R^2=0.60).

5.3.2.2 Comparison of all the values measured by the four different methods

Table 26 shows the different percentages that each method could measure from the total amount of Mg (XRF).

Table 26: Proportion of measured Mg from the total amount (XRF)

	% Mg from the total amount of Mg, measured with XRF			
Indicators	**WA**	**M3**	**Cohex**	**KCl**
Mean	0.23	6.72	6.33	4.95
RSD	0.19	4.46	4.59	3.46
Median	0.18	5.14	4.71	4.05
Min	0.05	2.01	0.22	0.19
Max	1.17	29.41	18.45	14.88

The mean, median, min and max percentage values resulting from all the Mg determination methods showed the following order of measured magnitude: **WA < KCl < CoHex < M3**

The first statistical analysis was based on all the data. According to the Kolmogorov-Smirnov test, the distribution of the data was not normal. This is why the non-parametric, Friedman's Two-way analysis of variance by ranks (ANOVA) test was used. The results of the statistical analysis proved that all the results of the applied methods provided significantly different results (Fr=181.766, df=3, p<0.0001) except for M3 and CoHex methods were not significantly different. (Figure 12)

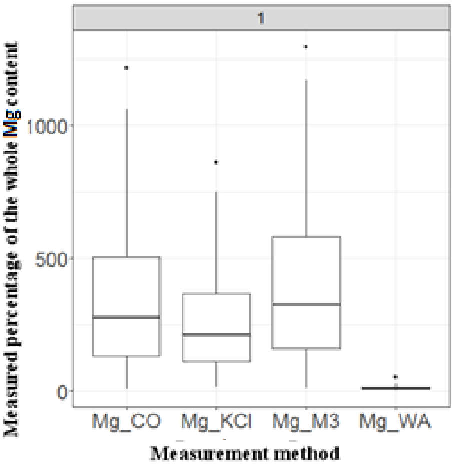


Figure 12: Results of the Boxplot analyses of four different Mg-extraction methods based on the percentage that each method could measure from the total amount of Mg, measured by a fifth method (XRF) (WA = water soluble, M3 = Mehlich 3, CO = Cobalt hexamine, KCl= Potassium Chloride)

Table 27: Results of statistical analyses of four different Mg-extraction methods based on the percentage that each method could measure from the total amount of Mg, measured by a fifth method (XRF)

Methods	**significance level**
WA vs. M3	**p < 0.001**
WA vs. CoHex	**p < 0.001**
WA vs. KCl	**p < 0.001**
M3 vs. CoHex	p = 0.521
M3 vs. KCl	**p < 0.001**
CoHex vs. KCl	**p < 0.001**

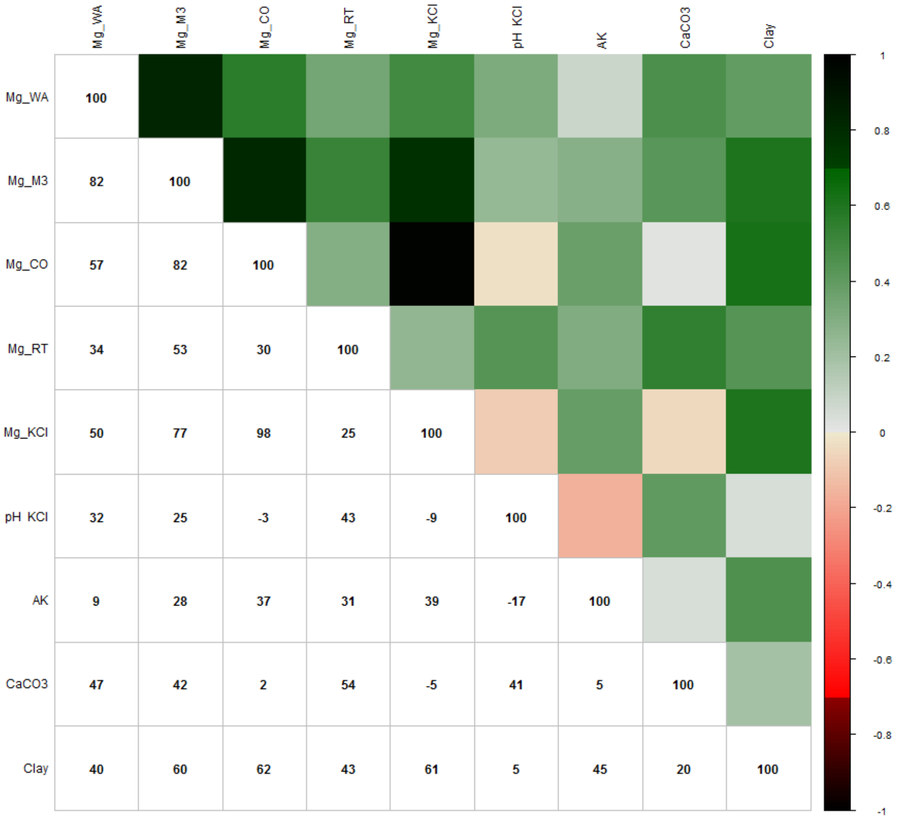
Table 27 shows that **all the methods are significantly different except for M3 vs CoHex.**

5.3.3 The effect of soil parameters on the Mg analyses methods

5.3.3.1 Pearson correlation analysis

Investigating the pH (KCl), $CaCO_3$-content, liquid limit according to Arany, clay content dependence, Pearson correlation analysis, and pairwise analysis tests were applied.

Figure 13 shows the results of the Pearson correlation analysis to get an overview of which soil parameters affect the amount of extracted magnesium of different analysis methods.



	Mg_WA	Mg_M3	Mg_CO	Mg_RT	Mg_KCl	pH KCl	AK	CaCO3	Clay
Mg_WA	100								
Mg_M3	82	100							
Mg_CO	57	82	100						
Mg_RT	34	53	30	100					
Mg_KCl	50	77	98	25	100				
pH KCl	32	25	-3	43	-9	100			
AK	9	28	37	31	39	-17	100		
CaCO3	47	42	2	54	-5	41	5	100	
Clay	40	60	62	43	61	5	45	20	100

Figure 13: Pearson correlation analysis (x*100) between the soil parameters and Mg analysis methods (red: darker the red weaker the correlation green: darker the green stronger the correlation)

Comparing the Mg analysis methods, there was a very strong correlation between M3 and WA (r=0.82), CoHex and M3 (r=0.82), KCl, and CoHex (r=0.98). A strong correlation was found between KCl and M3 (r=0.77) and a moderate correlation between CoHex and WA (r=0.57), XRF and M3 (r=0.53), KCl, and WA (r=0.50).

Evaluating the effect of soil parameters on the extracted magnesium, clay content showed a strong correlation with the analysis results of M3 (r=0.60), CoHex (r=0.62), and KCl (r=0.61) methods. The amount of

$CaCO_3$ content showed a moderate correlation with the amount of Mg that WA (r=0.47), M3 (r=0.42), XRF (r=0.54) methods measured. The pH(KCl) showed a moderate correlation with the Mg measurements of XRF (r=0.43) and a weak correlation with the analysis results of WA (32) and M3 (25), analysis methods. The KA values had a weak correlation with the amount of Mg that M3 (r=0.28), CoHex (r=0.37), XRF (r=0.31), and KCl (r=0.39) methods measured.

5.3.3.2 Evaluation of the measured Mg contents in the view of the influencing factors in the Hungarian advisory system

In the Hungarian advisory system, the liquid limit according to Arany is considered as the influencing factor for the availability of magnesium in the soil. The magnesium supply is classified based on 3 KA groups: <30 KA (n=0) 30-42 KA (n=58) and >42 KA (n=12). In the studied dataset there was no data in the group of <30 (Table 28).

Table 28: Proportion of measured Mg from the total amount (XRF) in case of 30-42 KA and >42 KA

		% Mg from the total amount of P (XRF)			
Indicators	**KA**	**Mg % WA**	**Mg M3**	**Mg CoHex**	**KCl**
Mean	**30-42**	**0.25**	**6.89**	**6.39**	**5.02**
	>42	**0.15**	**5.91**	**6.08**	**4.61**
RSD	**30-42**	0.20	4.79	4.91	3.72
	>42	0.06	2.21	2.70	1.87
Median	**30-42**	**0.21**	**5.01**	**4.54**	**3.41**
	>42	**0.15**	**5.70**	**5.60**	**4.58**
Min	**30-42**	0.05	2.01	0.22	0.19
	>42	0.05	2.65	2.06	1.46
Max	**30-42**	1.17	29.41	18.45	14.88
	>42	0.24	10.90	12.22	8.54

RSD – standard deviation

The mean, median, min and max percentage values resulting from the Mg determination methods showed the same order in the two Arany-type texture groups.

The order of the measured magnitude in case of **30-42 and >42 KA**:

WA < KCl < CoHex < M3 (Figure 14**)**

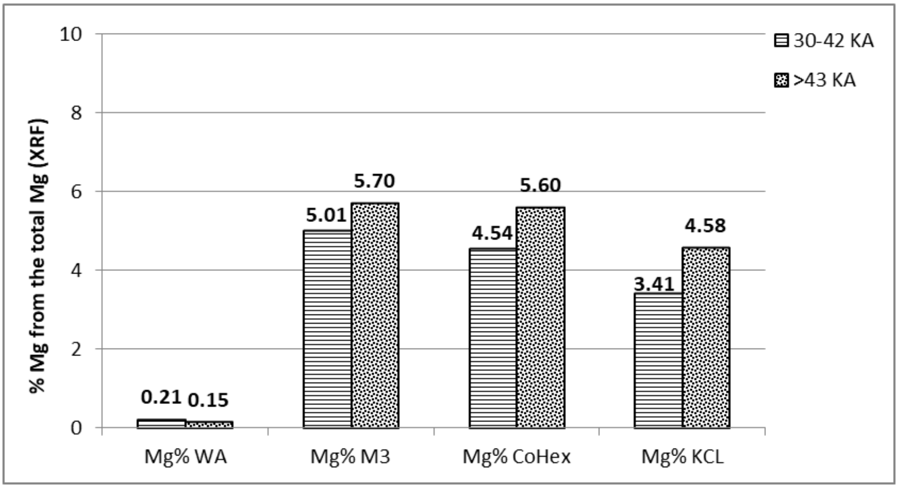


Figure 14: The median of the measured Mg % measured by the different amount from the total Mg (XRF) in case of 30-42 and >42 KA

In the case of >42 KA, the measured magnesium from the total was higher for M3, CoHex and KCl methods. In the case of WA, it is the other way around, >42 KA showed a lower amount of magnesium.

Linear regression with a significance level of 5% was used to determine the relationships of the soil Mg content measured by the WA, M3, CoHex and AL methods, according to the liquid limit according to Arany (Table 29).

Table 29: The linear regression with a significance level of 5% between the measured Mg percentages (from the total amount XRF) between the different analysis methods in the two liquid limit according to Arany categories

	KA 30-42		**KA >42**	
Methods	**R^2**	**p**	**R^2**	**p**
WA vs M3	0.38	**p=0.003**	0.37	**p=0.037**
WA vs CoHex	0.12	**p=0.008**	0.30	p=0.064
WA vs KCl	0.12	**p=0.007**	0.32	p=0.053
M3 vs CoHex	0.66	**p<0.001**	**0.84**	**p<0.001**
M3 vs KCl	0.56	**p<0.001**	**0.74**	**p<0.001**
CoHex vs KCl	**0.94**	**p<0.001**	**0.89**	**p<0.001**

R^2 – the percentage of the variability explained by the model; p – significance level

Comparing the KCl method that is applied in the Hungarian advisory system with the other methods resulted in different linear relationships between the two texture groups.

In the sandy, loamy (KA 30-42) texture soil, CoHex and KCl Mg determination methods had the highest determination coefficient (R^2=0.94) explaining 94.1% variance, followed by M3 – CoHex pair with 66.3% and M3 – KCl with 56.3% variance explained. All other pairs had significant linear relationships but with a smaller percentage of explained variance. In clayey texture (KA>42) CoHex and KCl methods showed the highest determination coefficient (R^2=0.89) explaining 89% variance, followed by M3 – CoHex pair with 84% and M3 – KCl with 74% variance explained. Three out of six pairs had a higher determination coefficient in the category above KA >42.

Besides the liquid limit according to Arany, the importance of lime is also emphasized in the advisory. On strong calcareous soils, magnesium deficiency can appear. The effect of lime was evaluated based on 3 lime categories: <0.1 $CaCO_3$%, 0.1–4.9 $CaCO_3$% and 5.0–19.9 $CaCO_3$% (Table 30).

Table 30: Proportion of the measured Mg from the total amount (XRF) in case of <0.1 $CaCO_3$%, 0.1–4.9 $CaCO_3$% and 5.0–19.9 $CaCO_3$%.

		% Mg from the total amount of Mg, measured with XRF			
Indicators	**$CaCO_3$ w/w %**	**WA**	**M3**	**CoHex**	**KCl**
Mean	**0.1**	**0.26**	**6.99**	**7.43**	**6.25**
	0.1–4.9	**0.23**	**6.47**	**6.48**	**4.86**
	5.0–19.9	**0.19**	**6.73**	**3.74**	**2.45**
RSD	**0.1**	0.19	3.97	4.72	3.45
	0.1–4.9	0.12	3.52	4.64	3.48
	5.0–19.9	0.30	7.06	3.26	1.84
Median	**0.1**	**0.23**	**6.29**	**6.77**	**5.69**
	0.1–4.9	**0.19**	**4.79**	**4.61**	**3.37**
	5.0–19.9	**0.12**	**4.46**	**2.66**	**1.84**
Min	**0.1**	0.05	2.01	1.17	1.12
	0.1–4.9	0.09	2.45	1.64	1.24
	5.0–19.9	0.06	2.62	0.22	0.19
Max	**0.1**	0.94	15.78	18.39	13.89
	0.1–4.9	0.63	16.39	18.45	14.88
	5.0–19.9	1.17	29.41	12.03	6.59

The mean, median, min and max percentage values resulting from the Mg determination methods showed the same order in the three $CaCO_3$ groups:

WA < KCl < CoHex < M3 (Figure 15).

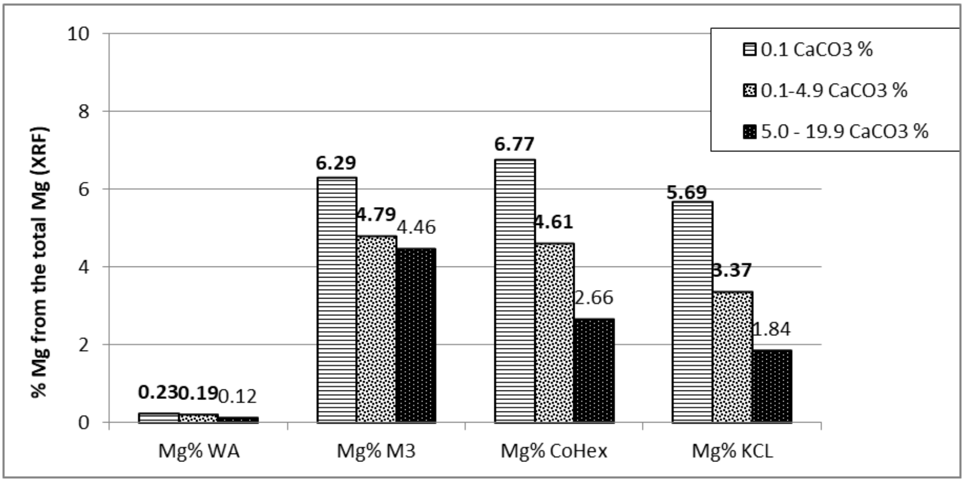


Figure 15: The median of the measured Mg % measured by the different amount from the total Mg (XRF) in case of <0.1 CaCO3%, 0.1–4.9 $CaCO_3$% and 5.0–19.9 $CaCO_3$%.

Higher lime content resulted in lower magnesium content extracted by the four methods. Lime had a smaller effect on M3 methods. The differences in magnesium measurements of WA and M methods in the different $CaCO_3$ categories were less remarkable while in case of the KCl and CoHex method the $CaCO_3$ content was much smaller in calcareous soil than in lime-free soils.

The effect of $CaCO_3$ content was also investigated with linear regression analysis that is presented in table 31.

Table 31: The linear regression with a significance level of 5% between the measured Mg percentages (from the total amount XRF) of the different analysis methods in the three lime categories.

	0.1		**0.1–4.9**		**5.0–19.9**	
Methods	**R^2**	**p**	**R^2**	**p**	**R^2**	**p**
WA vs. M3	0.06	p=0.208	0.23	**p=0.007**	**0.97**	**p<0.001**
WA vs. CoHex	0.09	p=0.632	0.19	**p=0.017**	0.65	**p=0.001**
WA vs. KCl	0.03	p=0.392	0.24	**p=0.006**	0.53	**p=0.005**
M3 vs. CoHex	**0.92**	**p<0.001**	**0.88**	**p<0.001**	**0.72**	**p<0.001**
M3 vs. KCl	**0.95**	**p<0.001**	**0.84**	**p<0.001**	0.62	**p=0.001**
CoHex vs. KCl	**0.95**	**p<0.001**	**0.95**	**p<0.001**	**0.96**	**p<0.001**

R^2 – the percentage of the variability explained by the model; p – significance level

In all lime categories, the linear relationship between CoHex vs KCl methods was significant, explaining more than 95% variance (R^2>0.95 p<0.001).

The measurement results of other methods were more dependent on the lime category. The higher $CaCO_3$-content showed a lower determination coefficient in case of M3 vs CoHex and M3 vs KCl methods.

The results of WA vs M3, WA vs CoHex and WA vs KCl pairs showed opposite results; in lime-free soils, there was no significant relationship between these methods, but the higher lime content ($CaCO_3$%>0.1) resulted in a significant linear relationship and higher determination coefficient.

In the highest lime content, these pairs showed significant linear relationships with determination coefficients from 0.53 up to 0.97.

5.3.3.3 Evaluating the effect of soil parameters with pairwise analysis

Further investigating the effect of soil parameters, pairwise analysis test, a type of location test that was used to compare measurements of the four magnesium analyses methods to assess whether their means differed. The proportions of measured Mg from the total amount (XRF) were used in the comparison and they were grouped according to specified pH, $CaCO_3$ content, liquid limit according to Arany, and clay content groups.

Comparison of the measured values in the classic pH groups

Group 1: In the first pH group (pH 3.39–4.35) the results of the CoHex method did not differ significantly from the other methods. There was no significant difference between M3 vs KCl and M3 vs CoHex. WA method did not differ significantly from CoHex but differed significantly from M3 and KCl. (Table 32).

The other methods are significantly different from each other (Table 33).

Group 2: In the second pH group (pH4.36–5.47) WA method measured significantly different Mg compared to the other three methods. The results of the M3 and CoHex methods were also significantly different. There was no significant difference between the results of M3 vs KCl and CoHex vs KCl (Table 32).

Group 3: In the third pH group (pH 5.48–6.78) WA method also measured significantly different Mg compared to the other three methods. There was no significant difference between the following pairs: M3 vs CoHex, M3 vs KCl, CoHex vs KCl (Table 32).

Group 4: In the fourth group (pH 6.79–7.2) only one pair was not significantly different; the results of M3 and CoHex methods. All the other pairs resulted in significant differences (Table 32).

Group 5: In the fifth group (7.21–8.14) all the different analysis methods were significantly different from each other (Table 32).

Table 32: Results of the pairwise analysis of the measured magnesium percentages compared with the measured total magnesium amounts based on the pH(KCl) group

	Group 1	**Group 2**	**Group 3**	**Group 4**	**Group 5**
pH(KCl)	3.39-4.35	4.36-5.47	5.48-6.78	6.79-7.2	7.21-8.14
WA vs. M3	**p<0.05**	**p<0.001**	**p<0.01**	**p<0.001**	**p<0.001**
WA vs. CoHex	p=0.053	**p<0.001**	**p<0.01**	**p<0.01**	**p<0.001**
WA vs. KCl	**p<0.05**	**p<0.001**	**p<0.01**	**p<0.01**	**p<0.001**
M3 vs. CoHex	p=0.491	**p<0.05**	p=0.443	p=1	**p<0.01**
M3 vs. KCl	p=0.828	p=0.217	p=0.084	**p<0.001**	**p<0.001**
CoHex vs. KCl	p=0.439	**p<0.01**	p=0.126	**p<0.01**	**p<0.001**

Based on the pH (KCl) groups we can conclude that WA vs M3 and WA vs KCl methods showed the biggest differences, these were significantly different in all pH groups.

In the strong acid pH group, the differences between the methods are less significant compared to the direction of neutral and alkaline groups.

It can be concluded that in the strong acid soils (pH 3.39-4.35) there were less significant differences compared to the pH range of 6.79-7.2 and 7.21–8.14. There was one exception, there was no significant difference between the results of M3 and CoHex methods in the fourth pH group.

The least number of significant differences was between M3 vs CoHex and M3 vs KCl methods. These were the most ‘similar’ methods.

Comparison of the measured values based on the $CaCO_3$-content groups

Group 1–2: In the first two $CaCO_3$ groups (<0.1 and 0.11–0.84%) there was no significant difference between M3 and CoHex method, all the other methods were significantly different from each other (Table 33).

Group 3: In the third group ($CaCO_3$ between 0.85 and 3.16%) there were no significant differences between the methods (Table 33).

Group 4: In the fourth group ($CaCO_3$ between 3.17 and 7.02%) there was no significant difference between the results of the M3 and CoHex method, the other pairs were significantly different. (Table 33).

Group 5: In the fifth group ($CaCO_3$ between 8.79 and 18.71%) there was no significant difference between the results of M3 vs KCl and M3 vs CoHex method. WA was significantly different from M3, CoHex and KCl. The results of magnesium measurements measured by Cohex and KCl were also significantly different (Table 33).

Table 33: Pairwise analysis of the measured magnesium percentages compared with the measured total magnesium amounts based on the $CaCO_3$ groups

	Group 1	**Group 2**	**Group 3**	**Group 4**	**Group 5**
$CaCO_3$ w/w %	<0.1	0.11–0.84	0.85–3.16	3.17–8.79	8.80–18.71
WA vs. M3	**$p < 0.001$**	**$p < 0.001$**	$p = 0.075$	**$p < 0.01$**	**$p < 0.01$**
WA vs. CoHex	**$p < 0.001$**	**$p < 0.01$**	$p = 0.163$	**$p < 0.05$**	**$p < 0.001$**
WA vs. KCl	**$p < 0.001$**	**$p < 0.001$**	$p = 0.23$	**$p < 0.05$**	**$p < 0.01$**
M3 vs. CoHex	$p = 0.188$	$p = 0.592$	$p = 1$	$p = 0.179$	$p = 0.265$
M3 vs. KCl	**$p < 0.001$**	**$p < 0.01$**	$p = 0.206$	**$p < 0.05$**	$p = 0.061$
CoHex vs. KCl	**$p < 0.01$**	**$p < 0.05$**	$p = 0.154$	**$p < 0.05$**	**$p < 0.01$**

In the lime-free or low calcareous soils, there are significant differences between all methods except M3 vs CoHex methods. In the third carbonate group ($CaCO_3$ 0.85–3.16%) there was no significant difference between the methods. The most obvious differences are between WA vs M3, CoHex, KCl methods. The less significant differences were between the results of the M3 and CoHex method.

Comparison of the measured values based on the liquid limit according to Arany groups

Group 1–2*:* In the first two Arany-type texture groups, in sandy loam texture (32–37 Arany type index) the following pairs did not differ significantly: M3 and CoHex, M3 and KCl, CoHex and KCl. All other pairs are significantly different (Table 34).

Group 3: In the third group (38) none of the pairs were significantly different (Table 34).

Group 4: In the fourth group (39–40), all the pairs were significantly different except the results of M3 vs CoHex (Table 34).

Group 5: In the fifth group (41), there was a significant difference between the following two pairs: M3 vs CoHex and M3 vs KCl. Mg measurement with WA extraction was significantly different from all other methods. CoHex method also differed significantly from KCl (Table 34).

Group 6: In the sixth group (42), the following pairs were not significantly different: WA vs KCl, M3 vs CoHex, M3 vs KCl, CoHex vs KCl. WA was significantly different from M3 and CoHex methods.

In the seventh group (43–44), the not significantly (M3 – CoHex, M3-KCl) and significantly different pairs (WA - M3, WA – CoHex, WA – KCl, CoHex – KCl) were the same as in group 5 (Table 34).

Group 8: In the eighth group (45-51) in the clayey loam, clay texture there were no significant differences between the results of the methods (Table 34).

Table 34: Pairwise analysis of the measured magnesium percentages compared with the measured total magnesium amounts based on the Arany-type (KA) texture groups

	Group 1	**Group 2**	**Group 3**	**Group 4**
KA	32-34	35-37	38-38	39-40
WA vs. M3	**$p < 0.05$**	**$p < 0.05$**	$p = 0.23$	**$p < 0.001$**
WA vs. CoHex	**$p < 0.05$**	**$p < 0.05$**	$p = 0.4$	**$p < 0.001$**
WA vs. KCl	**$p < 0.01$**	**$p < 0.05$**	$p = 0.208$	**$p < 0.001$**
M3 vs. CoHex	$p = 0.379$	$p = 1$	$p = 1$	$p = 1$
M3 vs. KCl	$p = 0.311$	$p = 0.38$	$p = 0.55$	**$p < 0.01$**
CoHex vs. KCl	$p = 1$	$p = 0.106$	$p = 1$	**$p < 0.01$**

	Group 5	**Group 6**	**Group 7**	**Group 8**
KA	41-41	42-42	43-44	45-51
WA vs. M3	**$p < 0.01$**	**$p < 0.05$**	**$p < 0.05$**	$p = 0.149$
WA vs. CoHex	**$p < 0.01$**	**$p < 0.05$**	**$p < 0.01$**	$p = 0.212$
WA vs. KCl	**$p < 0.01$**	$p = 0.056$	**$p < 0.05$**	$p = 0.127$
M3 vs. CoHex	$p = 1$	$p = 0.63$	$p = 1$	$p = 1$
M3 vs. KCl	$p = 0.17$	$p = 1$	$p = 0.218$	$p = 0.708$
CoHex vs. KCl	**$p < 0.01$**	$p = 0.083$	**$p < 0.05$**	$p = 0.738$

The influencing factor, Arany-type texture resulted in less significant differences between M3 vs Cohex, M3 vs KCl and CoHex vs KCl methods.

The most ‘similar’ methods were M3 vs CoHex and M3 vs KCl.

In all Arany-type categories, M3 and CoHex method was not significantly different from each other. M3 and KCl methods were also not different in all KA categories except Group 3 (39-40).

The most significant differences were between WA versus other methods.

Despite the differences, there was no significant difference in the third (KA 38) group which belongs to loam texture and in the eighth KA group which is clayey loam (KA 45<) according to the Hungarian Arany-type texture classification.

According to the Hungarian classification of liquid limit according to Arany group 1-2 (KA 32-37) belongs to the same category (KA 30-37) which is sandy loam. In both categories, the same 3 pairs were significant and the same three pairs were not significant. Group 3-6 belongs to one category according to the Hungarian classification, which is the loam. The null hypothesis was that in these groups there are similar results of the pairwise analysis but there were several differences in the results between the groups:

1. in group 3 none of the pairs were significantly different while
2. in group 4 almost all the methods differed significantly just M3 vs CoHex did not,
3. in group 5 only M3 vs Cohex and M3 vs KCl were not significantly different, all the other pairs differed significantly,
4. n group 6, only the results of WA vs M3 and WA vs Cohex method were significantly different.

So, after all, it cannot be concluded that the “behavior” of the measurements is the same, even in the same textural classes.

Comparison of the measured values based on the clay-content groups

Group 1: In the first clay group (6.82–9.64%) only WA was different from KCl and the other pairs did not differ significantly. (Table 35).

Group 2-3: In the second and third clay groups (10–12.74% and 12.99–15.69%) all the methods were significantly different except for M3 vs CoHex (Table 35).

In the fourth and fifth clay group (15.99–18.59%, 19.16–21.82%) M3 was not different from KCl and CoHex method. There was no significant difference between CoHex and KCl method. CoHex method measured significantly different Mg content compared to KCl. WA was significantly different compared to all the other methods.

Group 6: In the sixth clay group (21.83–24.89) M3 did not differ from CoHex and CoHex did not differ from KCL method significantly. The results of WA was significantly different compared to all the other methods.

Table 35: Pairwise analysis of the measured magnesium percentages compared with the total magnesium amounts (XRF) based on the clay content groups

	Group 1	**Group 2**	**Group 3**
Clay v/v %	6.82–9.64	9.65–12.74	12.75–15.69
WA vs. M3	p = 0.087	**p < 0.001**	**p < 0.001**
WA vs. CoHex	p = 0.087	**p < 0.001**	**p < 0.01**
WA vs. KCl	**p < 0.05**	**p < 0.001**	**p < 0.01**
M3 vs. CoHex	p = 0.942	p = 1	p = 1
M3 vs. KCl	p = 0.654	**p < 0.01**	**p < 0.05**
CoHex vs. KCl	p = 0.918	**p < 0.05**	**p < 0.05**

	Group 4	**Group 5**	**Group 6**
Clay v/v %	15.70–18.59	18.60–21.82	21.83–24.89
WA vs. M3	**p < 0.001**	**p < 0.01**	**p < 0.05**
WA vs. CoHex	**p < 0.001**	**p < 0.01**	**p < 0.05**
WA vs. KCl	**p < 0.001**	**p < 0.01**	**p < 0.05**
M3 vs. CoHex	p = 1	p = 1	p = 1
M3 vs. KCl	p = 0.066	p = 0.115	p = 1
CoHex vs. KCl	**p < 0.001**	**p < 0.05**	p = 0.115

There was no significant difference between M3 and CoHex method, they were ‘similar’ (not only nonsignificant but p was 1 in all cases except for one case but even here the p was 0.942, so close to one) in all clay categories. M3 and KCl methods did not differ significantly in the lowest clay content group and from 15.70% clay content.

The smallest clay content resulted in the smallest number of differences, while the most numerous significant differences were between 9.65 and 15.69% clay content. WA method was significantly different from the other methods in all clay groups except from Group 1. Overall, small clay content resulted the least differences between the methods.

All-inclusive evaluation of the effect of soil parameters on magnesium measurements

Summarizing the effect of the soil parameters on Mg measurements, it was calculated that how many percentages of the results of the pairwise analysis were significant

along with the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay) (Table 36).

It helped to evaluate the methods and establish general order.

Table 36: the average of the number of significant results of all the pairwise analysis of the Mg% measurements along with the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay).

	% of the significant results					
Methods	pH	$CaCO_3$	KA	Clay	**Average**	**ORDER**
M3 vs. CoHex	40	0	0	0	**10**	**1**
M3 vs. KCl	40	60	12.5	0	**28.1**	**2**
CoHex vs. KCl	60	80	37.5	33.3	**52.7**	**3**
WA vs. CoHex	80	80	75	50	**71.3**	**4**
WA vs. KCl	100	80	62.5	50	**73.1**	**5**
WA vs. M3	100	80	75	50	**76.3**	**6**

av: the average of the significant results

Order: evaluation from 1 to 6 (1: smallest different 8: biggest difference based on all parameters (pH+$CaCO_3$+KA+Clay)

Based on the average of the significance levels of all the pairwise analysis results along with the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay) the biggest number of non-significantly different results belonged to M3 vs CoHex method. There were only two significant differences between their results in the pH group 2 (pH 4.36–5.47) and 5 (pH 7.21–8.14), all the other results of the pairwise comparison were not significantly different.

Even though the results of the statistical analysis of the overall, all-inclusive data Table 27 showed that all the methods are significantly different expect for M3 vs Cohex, the detailed analysis of the categories of pH, $CaCO_3$, KA and clay resulted in different outcomes: more methods were not significantly different.

The smallest difference was between the results of M3 vs CoHex methods. M3 and KCl methods showed the least number of significant differences in the KA and Clay classification while M3 and KCl showed the least significant differences in pH and $CaCO_3$ classification.

WA method measured a significantly different amount of magnesium compared to the other 3 methods.

Evaluating the differences based on all parameters the following order can be made (1 - smallest difference 6 - biggest difference):

1. **M3 vs CoHex**
2. **M3 vs KCl**
3. **CoHex vs KCl**
4. **WA vs CoHex**
5. **WA vs KCl**
6. **WA vs M3**

Evaluating the differences based on all parameters it can be concluded that M3 vs CoHex were not significantly different from each other. The highest significant difference was between the results of P-WA vs M3 method.

5.3.4 Discussions concerning magnesium measurements

There are several soil analysis methods used for predicting the phytoavailability of the nutrients, making a direct comparison of the results often difficult (RICE and KAMPRATH 1968; GRANSEE and FÜHRS 2013). In this comparative analysis study, difficulties were also found. The data analyses proved that there were significant differences between the methods. A comparison of methods with linear regression showed an unexpected strong relationship (R^2=0.96) between the KCl and CoHex methods based on percentage of the variability (R^2) However, these two methods should be more dissimilar from one another as the KCl method "only" measures the soluble and the readily exchangeable part of the Mg in the soil, while the CoHex method can also measure the slowly exchangeable part. The KCl and M3 methods were expected to produce similar results with a high determination coefficient, but they showed a weaker relationship (R^2=0.60). The M3 and CoHex methods had a similar low determination coefficient of 0.66.

The complexity of a soil analysis was proven by STAUGAITIS AND RUTKAUSKIENĖ (2010) who compared six different Mg extraction and determination methods and found that the extraction procedure strongly impacts the outcome, similarly seen in this study. Nevertheless, all mild extraction procedures including $CaCl_2$, KCl, NH_4OAc and the M3 method showed quite high correlations over all three sampling depths investigated, indicating similar extraction characteristics for the soil Mg. These results do not reflect our findings where the KCl extraction resulted in much lower amounts, compared to those of the M3 method. A comparison of methods showed expected differences between the KCl and CoHex methods (as the KCl method measures significantly lower amounts) with the Wilcoxon signed-rank test, since KCl does not bring the slowly exchangeable Mg into the solution, so it does not measure it. The basic statistical figures of the mean and median values produced the same order of magnitude for the methods; the WA method measured the smallest, then KClmethod the middle range then followed by CoHex method then with M3. In the results of a joint institutional project in Czechia, Hungary, Poland and the Netherlands on the calibration of the 0.01M $CaCl_2$ soil testing procedure for Mg are presented by LOCH et al. (1998) with the relatively weak extractant, 0.01M CaCl2, somewhat lower quantities of Mg were extracted from the soil samples compared to the extraction solutions used in Poland (0.0125M $CaCl_2$), in Hungary (1M KCl) and in the Netherlands (0.5M NaCl). With the relatively strong extractant used in Czechia (Mehlich II), more Mg was extracted. Based on the study of ZBÍRAL and NĚMEC (2000), significant correlations were found between the M2 and M3 methods for all the nutrients (the correlation coefficients were in the range of 0.97–0.99). This result corresponds with our findings where the M3 method measured more Mg than the KCl method. In general, the amount of Mg extracted increases, i.e., 0.01 M CaCl2 < Schachtschabel < Mehlich-2. The previously mentioned and this study’s results show the importance of choosing an appropriate extraction method for the correct evaluation of the soil Mg availability to the crops. The amount of Mg that can be extracted from the soils depends on the chemical composition and concentration of the extracting solution in combination with the ratio of the soil-to-extracting-solution (LOCH 1970). The readily soluble Mg-containing solid constituents and Mg bound to the cation exchange complex of the soil is regarded as the plant available fraction. Extraction of the soil elements with unbuffered soil solutions like 1M KC1 (MAZAEVA 1967) is used to extract this plant-available fraction from the soil. The use of acidic extractants is not advised because they also extract part of the Mg reserves of the soil. Despite this, Mehlich (1978; 1984) developed a multinutrient extractant, buffered at pH = 2.5, for the determination of the plant-available soil fractions of Mg (LOCH 1970). The applied Mg availability categories are theoretical since RICE and KAMPRATH (1968) found a large amount of Mg uptake by maize from the nonexchangeable pool. This strengthens the need to re-establish the limit between the readily available Mg and the nonexchangeable Mg pool for agricultural plants. The Mehlich-2 method also extracts part of the Mg reserves of the soil, especially in soils containing dolomite (LOCH 1970). The acidified extractants may promote the dissolution of structural forms like Mg containing carbonates and minerals (SPOSITO 1994). In our study, it was also visible that the M3 method extracted more Mg compared to the KCl method. In most comparative studies, the results of the two extraction procedures are related by using statistical techniques like (multiple) linear regression. To increase the explained variance of the relationships, soil characteristics like the soil type, organic matter, clay, and carbonate contents are also arbitrarily included (BAIER and BAIEROVA 1981; MATEJOVIC and DURACKOVA 1994; MAMO et al. 1996; LOCH et al. 1998). We can also conclude that not only the extraction method, but also soil properties like the carbonate content, have an effect on the evaluation of the magnesium measurements. Our results showed that, in the case of the $CaCO_3$ free or low $CaCO_3$-content soils, there was strong relationship between the three methods, but the increased $CaCO_3$ content showed weaker correlations. Van Erp (2002) compared the relationship between

0.01 M CaCl2, $BaCl_2$ and KCl extractants. An analysis of the difference in the Mg extracted among the $BaCl_2$ and KCl methods showed that the difference was related to the clay content of the soils and not to the organic C content or carbonate content. The Mg was specifically adsorbed at the surface of these (hydr)oxides which is not replaceable by K at a high pH (CHAN et al. 1979). DONTSOVA and NORTON (2002) reported on the degrading effect of a high Mg content on the soil structure and clay dispersion. Contrarily, WANG et al. (2004) found no texture effect on the Mg availability. ORTAS et al. (1999) state that there is often a poor relationship between the plant growth response and extractable nutrients in the soil. A soil analysis just provides a picture of the current situation at a given site; it is not capable of perfectly simulating the plant characteristics on the Mg uptake. Also, other agronomic and environmental factors are not included. Consequently, a soil analysis only gives information on the potential of a soil to provide the respective nutrients (GRANSEE and FÜHRS 2013). Concerning the comparison and evaluation of the different Mg determination methods, it should be further investigated to find the most appropriate method for the different varieties of influential soil properties.

5.3.5 Conclusions concerning magnesium measurements

Physicochemical properties and the chosen classification method affected the evaluation of magnesium measurements.

Mehlich 3 solution demonstrated a greater capacity of extracting Mg from the soil, compared with other extract solutions.

Magnesium content measured by the four methods resulted in the following order: **WA < KCl < CoHex < M3 < XRF**

The linear regression between all the pairs of Mg content measurement methods are significant, but only 4 of them explain more than 60% of the total variation. The linear relationship between KCl and CoHex methods has the highest determination coefficient (R^2=0.96), followed by WA – M3 (R^2=0.68), M3 – CoHex (R^2=0.66) and M3 – KCl (R^2=0.60).

CoHex vs KCl methods showed an unexpectedly strong relationship. However, these two methods should be more dissimilar from one another as the KCl method “only” measures the soluble and the readily exchangeable part of the Mg in the soil, while the CoHex method can also measure the slowly exchangeable part.

The KCl and M3 methods were expected to produce similar results with a high determination coefficient, but they showed weaker relationship (R^2=0.60). The M3 and CoHex methods had a similar low determination coefficient of 0.66.

The results of the pairwise analysis based on the percentage that each method could measure from the total amount of Mg (XRF) proved that **all the methods were significantly different except for M3 and CoHex methods.**

Pairwise analysis of the measured magnesium percentages compared with the total magnesium amounts (XRF) based on the Arany-type classification showed that in clayey loam texture (42–51 KA), the measured magnesium contents of each method was higher compared to the sandy texture.

Comparing the KCl method that is applied in the Hungarian advisory system with the other methods resulted in different linear relationships between the two texture groups. In the sandy, loamy texture (KA 30-42) texture soil, CoHex and KCl Mg determination methods had the highest determination coefficient (R^2=0.94) explaining 94.1% variance, followed by M3 – CoHex pair with 66.3% and M3 – KCl with 56.3% variance explained. All other pairs had significant linear relationships but with a smaller percentage of explained variance.

The effect of lime content on magnesium measurement methods were also investigated.

Higher lime content resulted in lower extracted magnesium by the four methods.

In all lime categories, the linear relationship between CoHex vs KCl methods was significant, explaining more than 95% variance (R^2>0.95 $p<0.001$).

The relationships between the measurement results of the other methods (WA vs. M3, WA vs. CoHex, WA vs. KCl, M3 vs. CoHex, M3 vs. KCl) were more dependent on the lime category.

The higher $CaCO_3$-content showed a lower determination coefficient in case of M3 vs CoHex and M3 vs KCl methods. The results of WA vs M3, WA vs CoHex and WA vs KCl pairs showed opposite results; in lime-free soils, there was no significant relationship between these methods, but the higher lime content ($CaCO_3\%>0.1$) resulted in a significant linear relationship and higher determination coefficient.

The further comparison of the methods based on the influencing factors, such as pH, lime content, texture class, and clay content showed the differences between the different methods.

Linear regression and Pearson correlation analysis showed the strongest correlation between CoHex and KCL.

The pairwise analysis showed other aspects. The pairwise analysis showed that the least significant differences were between the results of M3 vs Cohex and KCl vs M3 methods.

Evaluating the differences based on all parameters the following order can be made (1 - smallest difference 6 - biggest difference):

1. **M3 vs CoHex**
2. **M3 vs KCl**
3. **CoHex vs KCl**
4. **WA vs CoHex**
5. **WA vs KCl**
6. **WA vs M3**

Evaluating the differences based on all parameters it can be concluded that M3 vs CoHex were not significantly different from each other. The highest significant difference was between the results of P-WA vs M3 method.

5.4 Comparison of zinc determination methods

5.4.1 Descriptive statistics of the Zn analysis results

The descriptive statistics of the soil sample set are presented in Table 37. The basic statistical data of the soils' Zn contents determined by the different methods (n = 70)

Table 37: The basic statistical data of the soils as Zn contents determined by the different methods (No. of samples (n) = 70)

Indicators	**Zn content (mg/kg)**				
	WA	**M3**	**CoHex**	**EDTA**	**XRF**
Mean	0.07	2.69	0.31	2.03	58.91
SD	0.09	2.42	0.59	1.28	25.82
Median	0.05	2.15	0.05	1.70	62.11
CV	1.20	0.90	1.88	0.63	0.44
Min	0.04	0.60	0.01	0.41	0.43
Max	0.68	13.35	2.60	6.40	158.00

RSD – standard deviation; CV – coefficient of variation

The highest Zn content was measured by XRF analysis which determines the total amount of Zn in the soil. The other methods measured much less because these extracts dissolve less zinc and they are applied to represent the available zinc content in the soil. Comparing the four other methods, Cohex and WA showed the lowest whereas EDTA the highest zinc content in the soil.

The median of the Zn content measured by the four methods resulted in the following order:

CoHex ≤ WA < EDTA < M3 < XRF

The mean of the Zn content measured by the four methods resulted in the following order:

WA < CoHex < M3 < EDTA < XRF

5.4.2 Comparison of the different Zn analyses methods

5.4.2.1 Comparison of all the values measured by the five different methods

Firstly, linear regression with a significance level of 5% was used to determine the relationships of the soil Zn content measured by the Water, Mehlich 3, CoHex, KCl-EDTA and XRF methods, as it is shown in Table 38. The figures of the linear regression models are presented in Annex 3.

Table 38: The linear regression with a significance level of 5% between the Zn contents measured by WA, M3, CoHex, EDTA, XRF methods.

Methods	**R^2**	**p**
EDTA vs WA	0.21	**$p<0.001$**
EDTA vs M3	**0.71**	**$p<0.001$**
EDTA vs CoHex	0.14	**$p=0.002$**
EDTA vs XRF	0.09	**$p=0.012$**
WA vs M3	0.19	**$p<0.001$**
WA vs CoHex	0.05	$p=0.069$
WA vs XRF	0.05	$p=0.065$
M3 vs CoHex	0.01	$p=0.323$
M3 vs XRF	0.06	**$p=0.036$**
CoHex vs XRF	0.06	**$p=0.039$**

R^2 – the percentage of the variability explained by the model; p – significance level

The relationship between EDTA and M3 Zn determination methods explains 71% variation, all the other determination coefficients are lower than 0.2 or aren’t significant.

5.4.2.2 Comparison of all the values measured by the four methods

Table 39 and figure 15 shows the different percentages that each method could measure from the total amount of Zn (XRF).

Table 39: Proportion of measured Zn from the total amount (XRF)

Indicators	% from the total amount of Zn, measured with XRF			
	Zn% WA	**Zn% M3**	**Zn% CoHex**	**Zn% EDTA**
Mean	1.46	4.88	0.65	3.95
RSD	2.16	4.21	1.39	3.4
Median	0.86	3.98	0.08	3.28
Min	0.34	1.02	0.02	0.76
Max	13.83	27.71	8.81	24.62

The mean, median, min and max percentage values resulting from all the Zn determination methods showed the following order of measured magnitude:

CoHex < WA < EDTA < M3 < XRF.

The first statistical analysis was based on all the data. According to the Kolmogorov-Smirnov test, the distribution of the data was not normal. This is why the non-parametric, Friedman's Two-way analysis of variance by ranks (ANOVA) test was used. The results of the statistical analysis proved that all the applied methods provided different results, (Fr=181.766, df=3, p=0.000), the amounts of extracted Zn by the methods were different (Figure 16).

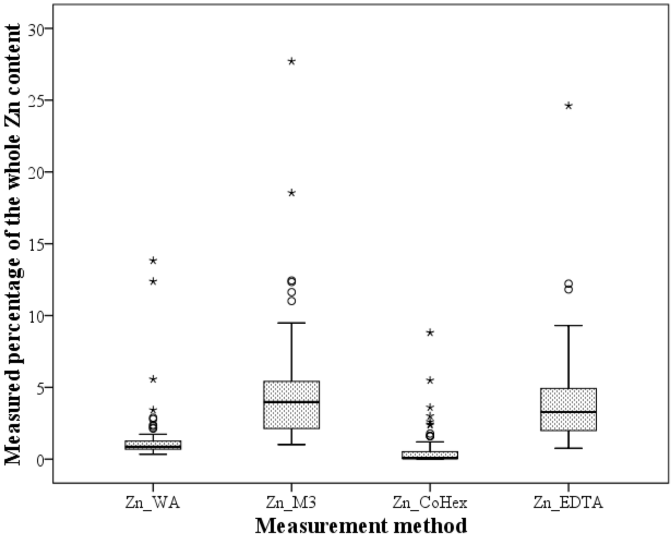


Figure 16: Results of the Boxplot analyses of four different Zn-extraction methods based on the percentage that each method could measure from the total amount of Zn, measured by a fifth method (XRF) (WA = water soluble, M3 = Mehlich 3, CoHex = Cobalt hexamine, EDTA = EDTA-KCl)

Table 40 shows that all the methods are significantly different. M3 vs EDTA methods showed the least significant difference ($p<0.046$).

Table 40: Results of statistical analyses of four different Zn-extraction methods based on the percentage that each method could measure from the total amount of Zn, measured by a fifth method (XRF)

Methods	**significance level**
CoHex vs. WA	**p<0.001**
CoHex vs. EDTA	**p<0.0001**
CoHex vs. M3	**p<0.0001**
WA vs. EDTA	**p<0.0001**
WA vs. M3	**p<0.0001**
EDTA vs. M3	**p<0.046**

5.4.3 The effect of soil parameters on the Zn analyses methods

5.4.3.1 Pearson correlation analysis for the total Zn-dataset

Investigating the pH (KCl), $CaCO_3$-content, liquid limit according to Arany, clay content dependence, Pearson correlation analysis, and pairwise analysis tests were applied.

Figure 17 shows the results of the Pearson correlation analysis to get an overview of which soil parameters affects the extracted zinc of different analysis methods.

	Zn WA mg/kg	Zn M3 mg/kg	Zn CoHex mg/kg	Zn EDTA mg/kg	Zn XRF mg/kg	pH(KCl)	AK	CaCO3 %	Clay %
Zn WA mg/kg	100								
Zn M3 mg/kg	44	100							
Zn CoHex mg/kg	22	12	100						
Zn EDTA mg/kg	45	85	37	100					
Zn XRF mg/kg	-22	25	25	30	100				
pH(KCl)	-10	16	-68	-9	-5	100			
AK	-25	10	26	24	60	-17	100		
CaCO3 %	-12	8	-20	-13	-4	41	5	100	
Clay %	-17	8	18	16	55	5	45	20	100

Figure 17: Pearson correlation analysis (x*100) between the soil parameters and Zn analysis methods (red: darker the red weaker the correlation green: darker the green stronger the correlation)

Comparing the Zn analysis methods, there was a very strong correlation between EDTA and M3 (r=0.85) methods. WA with EDTA (r=0.45) and M3 (r=0.44) methods also showed a strong correlation.

Evaluating the effect of soil parameters on the extracted zinc, the XRF method showed a positive moderate correlation with clay (r=0.55) and a strong correlation with the liquid limit according to Arany (AK). pH showed a strong negative correlation with the CoHex method (r=-0.68).

5.4.3.2 Evaluation of the measured Zn contents in the view of the influencing factors in the Hungarian advisory system

In the Hungarian advisory system, the evaluation of zinc availability is based on the liquid limit according to Arany. The zinc supply is classified based on 3 KA groups: <38 KA (n=29), 38-50 KA (n=40) and >50 KA but in the studied dataset there was only one data in this third group >50 (n=1) which was added to the group of 38-50 KA (Table 41).

Table 41: Proportion of measured Zn from the total amount (XRF) in case of <38 KA and 38-50 KA

Indicators		% from the total amount of P, measured with XRF			
	KA	**Zn % WA**	**Zn% M3**	**Zn% CoHex**	**Zn% EDTA**
Mean	**<38**	**0.24**	**6.54**	**0.81**	**5.16**
Mean	**38-50**	**0.08**	**3.81**	**0.50**	**3.13**
RSD	**<38**	0.31	5.62	1.90	4.70
RSD	**38-50**	0.02	2.37	0.86	1.72
Median	**<38**	**0.14**	**4.63**	**0.08**	**3.65**
Median	**38-50**	**0.07**	**3.31**	**0.07**	**3.09**
Min	**<38**	0.05	1.61	0.01	1.16
Min	**38-50**	0.03	1.02	0.03	0.76
Max	**<38**	1.39	27.69	8.83	24.62
Max	**38-50**	0.16	11.01	3.61	6.75

The mean, median, min and max percentage values resulting from the Mg determination methods showed the same order in the two liquid limit according to Arany.

The order of the measured magnitude in case of <38 KA and 38–50 KA: **WA < CoHex < EDTA < M3** (Figure 18).

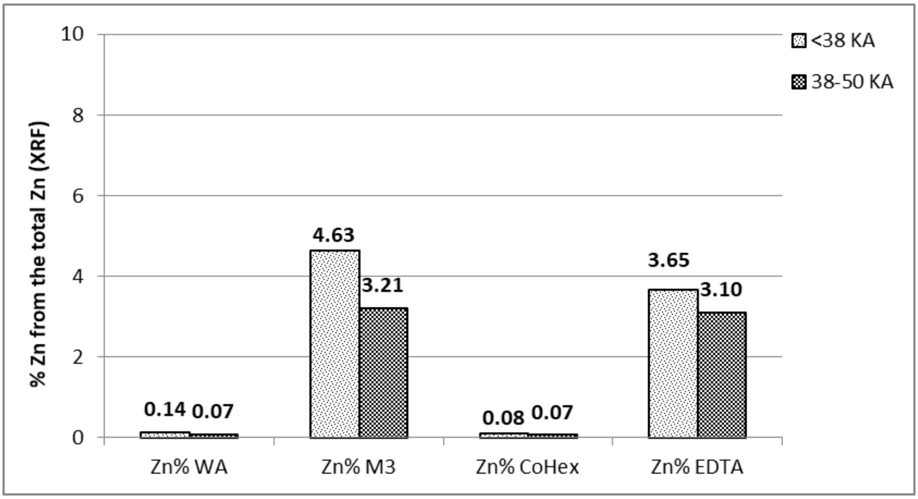


Figure 18: The median of the measured Zn% measured by the different amount from the total Zn (XRF) in case of <38 KA and 38-50 KA

In loam and clayey loam texture groups (38-50 KA), the measured zinc from the total was lower for all of the methods compared to the measurements in sandy loam texture.

The results of the correlation regression analysis determine the relationships of the soil Zn content measured by the WA, M3, CoHex and AL methods, according to the liquid limit according to Arany is shown in Table 42.

Table 42: The linear regression with a significance level of 5% between the measured Zn percentages (from the total amount XRF) and the different analysis methods in the two liquid limit according to Arany categories

	KA <38		**KA 38-50**	
Methods	**R^2**	**p**	**R^2**	**p**
CoHex vs. WA	0.47	**p<0.001**	0.09	p=0.059
CoHex vs. EDTA	0.12	p=0.071	0.14	**p=0.014**
CoHex vs. M3	0.04	p=0.274	0.01	p=0.589
WA vs. EDTA	0.67	**p=0.001**	0.18	**p=0.006**
WA vs. M3	0.51	**p<0.001**	0.26	**p<0.001**
EDTA vs. M3	**0.84**	**p<0.001**	**0.67**	**p<0.001**

R^2 – the percentage of the variability explained by the model; p – significance level

In the category of KA<38 EDTA and M3 methods of determining Zn have the highest determination coefficient explaining more than 84% of the total variation. EDTA vs WA relationship explains 67.3%, WA vs M3 50.6% and CoHex vs WA explains 47.4% of the total variance. In the category of KA 38-50 the determination coefficients between the pairs were smaller compared to the category of KA<38.

The linear relationship between the methods was much weaker in the case of loam/clayey loam soils.

5.4.3.3 Evaluating the effect of soil parameters on Zn measurements with pairwise analysis

Further investigating the effect of soil parameters, a pairwise analysis test, a type of location test was used to compare measurements of the four zinc analysis methods to assess whether their means differed. The proportions of measured Zn from the total amount (XRF) were used in the comparison and they were grouped according to specified pH, $CaCO_3$ content, liquid limit according to Arany, and clay content groups.

Comparison of the measured values in the classic pH groups

Group 1-2: In the first two pH (KCl) groups (3.39–4.35 and 4.36–5.47), based on the comparison between the groups M3 was not different from EDTA and WA was not different from CoHex, but the other pairs were significantly different (Table 43).

Group 3-4: In the third and fourth pH (KCl) group (5.48–6.78 and 6.79–7.2 there was a new pair that was not significantly different, not only M3 and EDTA, WA and CoHex were different but also WA and EDTA. All other pairs were different (Table 43).

Group 5: In the fifth pH (KCl) group (7.21–8.14) there was only one pair, that was not significantly different - M3 and EDTA. All the other pairs resulted in significant differences (Table 43).

Table 43: Pairwise analysis of the measured zinc percentages compared with the measured total zinc amounts based on the pH(KCl) groups

	Group 1	**Group 2**	**Group 3**	**Group 4**	**Group 5**
pH(KCl)	3.39-4.35	4.36-5.47	5.48-6.78	6.79-7.2	7.21-8.14
CoHex vsWA	p=1	p=1.000	p<0.347	p<0.290	**p<0.031**
CoHex vs EDTA	**p<0.01**	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**
CoHex vs. M3	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**
WA vs EDTA	**p<0.049**	**p<0.010**	p<0.068	p<0.201	**p<0.044**
WA vs M3	**p<0.003**	**p<0.010**	**p<0.009**	**p<0.001**	**p<0.001**
EDTA vs M3	p=1	p=1	p=1	p<0.568	p<0.113

Based on the pH (KCl) groups it can be concluded that there was no significant difference between **EDTA and M3** methods, these were ‘similar’ in all groups. Based on the p values the differences were the biggest between the **CoHex and the M3 methods.**

On the other hand, there was a clear trend: in the acid groups, the differences between the methods were less obvious compared to the direction of less acid and finally to the more alkaline groups. **We can conclude that measurements of Zn are less different in the case of acid soils** and significantly different in almost all the 7.21–8.14 range. There was one exception, the CoHex and M3 methods were showing a very strongly significant difference in all the groups. However, the p values are decreasing towards higher pH values that also underlines the observed trend even in this case.

The most obvious differences were between Cohex and M3 + CoHex and EDTA.

Comparison of the measured values based on the $CaCO_3$-content groups

Group 1–2: There was no significant difference between (0–0.84%) EDTA vs M3 and CoHex vs WA, the other methods were significantly different from each other (Table 44).

Group 3-4-5: (1.01–18.71%) EDTA did not differ from WA only from the CoHex method. WA and CoHex, M3 and EDTA were not significantly different. Significant differences were listed in Table 44.

Table 44: Pairwise analysis of the measured zinc percentages compared with the measured total zinc amounts based on the $CaCO_3$ groups

	Group 1	**Group 2**	**Group 3**	**Group 4**	**Group 5**
$CaCO_3$ w/w %	<0.1	0.11–0.84	0.85–3.16	3.17–8.79	8.80–18.71
CoHex vs. WA	p<0.439	p<0.169	p=1	p<0.500	p<0.865
CoHex vs. EDTA	**p<0.001**	**p<0.001**	**p<0.023**	**p<0.003**	**p<0.021**
CoHex vs. M3	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**
WA vs. EDTA	**p<0.001**	**p<0.040**	p<0.375	p<0.500	p<0.865
WA vs. M3	**p<0.001**	**p<0.001**	**p<0.023**	**p<0.003**	**p<0.006**
EDTA vs. M3	p=1.000	p<0.933	p=1	p<0.500	p<0.407

The order of differences in $CaCO_3$ groups is the same as in the case of pH(KCl), there is only a slight difference, the strength of the difference between the WA and M3 is slightly stronger than between CoHex and EDTA in the case of $CaCO_3$ than in case of pH(KCl).

The reason for this change is that the significance of the difference in the biggest $CaCO_3$ category (8.8–18.71%) between WA and M3 is stronger (p<0.006) than in the case of CoHex and EDTA (p<0.021). Furthermore, the number of non-significant differences is bigger in the case of the comparison of the measured values with increasing $CaCO_3$ amounts. So, overall, we can conclude that **the methods are more different in the case of smaller lime content and getting less different with increasing lime content.**

Comparison of the measured values based on the liquid limit according to Arany groups

Group 1–5: In the first five Arany-type texture groups, from sandy loam to loam texture (KA=32–41) **Az M3 vs EDTA, EDTA vs WA, WA vs CoHex were not different.** All other pairs are significantly different (Table 45).

Group 6: In the sixth group (KA=42) M3 did not differ from EDTA and CoHex, EDTA did not differ from CoHex and Co-Hex did not differ from WA. Just WA differed significantly from M3 and EDTA (Table 45).

Group 7: In the seventh group (KA=43–44) EDTA was not significantly different from the other methods, WA did not differ from CoHex but M3 was significantly differed from WA and CoHex. (Table 45).

Group 8: In the eighth group (KA=45–51) four methods were significantly different: WA vs M3, WA vs EDTA, M3 vs CoHex, EDTA vs CoHex. WA vs CoHex and M3 vs EDTA methods were not significantly different (Table 45).

Table 45: Pairwise analysis of the measured zinc percentages compared with the measured total zinc amounts based on the Arany-type texture groups.

Methods	**Group 1**	**Group 2**	**Group 3**	**Group 4**
AK	32–34	35–37	38–38	39–40
CoHex vs. WA	p<0.191	p<0.285	p<0.728	p<0.342
CoHex vs. EDTA	**p<0.002**	**p<0.002**	**p<0.003**	**p<0.001**
CoHex vs. M3	**p<0.001**	**p<0.001**	**p<0.001**	**p<0.001**
WA vs. EDTA	p<0.823	p<0.592	p<0.317	p<0.115
WA vs. M3	**p<0.018**	**p<0.006**	**p<0.040**	**p<0.002**
EDTA vs. M3	p<0,823	p<0,592	p=1	p=1

Methods	**Group 5**	**Group 6**	**Group 7**	***Group 8**
AK	41–41	42–42	43–44	45–51
CoHex vs. WA	p<0.500	p=1	p=1	p=1
CoHex vs. EDTA	**p<0.001**	p<0.165	p<0.083	**p<0.05**
CoHex vs. M3	**p<0.001**	p<0.300	**p<0.005**	**p<0.05**
WA vs. EDTA	p<0.226	**p<0.020**	p<0.265	**p<0.05**
WA vs. M3	**p<0.011**	**p<0.042**	**p<0.022**	**p<0.05**
EDTA vs. M3	p=1	p=1	p=1.000	p=1

*Group 8: The results of the Tukey post hoc test

The influencing factor, Arany-type texture resulted in less significant differences between the groups. In this case, there were only significant differences in all the groups between the WA and M3 methods, and all other cases, there was at least one non-significant difference.

This is the first case when the **strongest difference** is not between the CoHex and M3 methods but **between the WA and M3 methods.**

In the Hungarian classification, Group 3-6 belongs to the same category, which is the loam. The null hypothesis was that in these groups there will be similar results but surprisingly there were significant differences between CoHex and EDTA, and CoHex and M3 in Group 3–5, there were none in Group 6, and vice versa. There were no significant differences in the case of WA and EDTA in Group 3–5 while there were in the case of Group 6. **So, after all, we cannot conclude that the "behavior" of the measurements is the same, even in the same textural classes.**

Comparison of the measured values based on the clay-content groups

Group 1: In the first clay group (6.82–9.64%) only CoHex was different from EDTA and CoHex was different from M3, the other pairs were not significantly different (Table 46).

Group 2-3: In the second and third clay groups (10–12.74% and 12.99–15.69%) the following two pairs were not significantly different: M3 vs EDTA and WA vs CoHex. All other pairs were significantly different (Table 46).

Group 4: In the fourth clay group (15.99–18.59%) EDTA is no longer different from WA, only there is a significant difference between the results of M3 and WA methods. CoHex method still differed significantly from M3 and EDTA (Table 46).

Group 5: In the fifth group (19.16–21.82%) only CoHex differed from EDTA and M3, the other pairs were not significantly different, just like in the first clay group (Table 46).

Group 6: In the sixth clay group (22.01–24.89%) M3 differed from WA and CoHex, the other pairs were not significantly different (Table 46).

Table 46: Pairwise analysis of the measured zinc percentages compared with the measured total zinc amounts based on the Clay groups

Clay v/v %	**Group 1** 6.82–9.64	**Group 2** 9.65–12.74	**Group 3** 12.75–15.69
CoHex vs. WA	p<0.199	p<0.113	p<0.859
CoHex vs. EDTA	**p<0.040**	**p<0.001**	**p<0.001**
CoHex vs. M3	**p<0.001**	**p<0.001**	**p<0.001**
WA vs. EDTA	p=1.000	p<0.007	p<0.008
WA vs. M3	p<0.121	**p<0.001**	**p<0.003**
EDTA vs. M3	p<0.488	p<0.561	p=1

Clay % v/v %	**Group 4** 15.70–18.59	**Group 5** 18.60–21.82	**Group 6** 21.83–24.89
CoHex vs. WA	p<0.568	p=1	p=1
CoHex vs. EDTA	**p<0.001**	**p<0.022**	p<0.518
CoHex vs. M3	**p<0.001**	**p<0.005**	**p<0.020**
WA vs. EDTA	p<0.059	p<0.265	p<0.300
WA vs. M3	**p<0.002**	p<0.083	**p<0.009**
EDTA vs. M3	p=1	p=1	p=1

Similar to the Arany-type texture groups, there is also only one case when all the groups resulted in significant differences and this case is between CoHex and M3. **The smallest clay content and the biggest clay content resulted in the smaller differences**, while the most numerous significant differences were between 10 and 15.69%. This is not following the trend that we observed with the texture groups. The biggest number of significant differences was in the most clayey texture group that is clayey-loam.

5.4.3.4 All-inclusive evaluation of the effect of soil parameters on zinc measurements

The analysis of the differences between the Zn measurement methods allows us to compare the differences and similarities, furthermore their strength with other soil parameters such as pH (KCl), texture, clay, and $CaCO_3$ content. This way we could establish trends or tendencies.

Summarizing the effect of the soil parameters, it was calculated that how many percentages of the results of the pairwise analysis were significant along with the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay) (Table 47).

Table 47: the average of the number of significant results of all the pairwise analysis of the Zn% measurements along with the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay).

	% of the significant results					
Methods	pH	$CaCO_3$	KA%	Clay	Average	**ORDER**
EDTA vs M3	0	0	0	0	**0**	**1**
CoHex vs WA	20	0	0	0	**5**	**2**
WA vs EDTA	60	40	25	33.3	**39.6**	**3**
WA vs M3	100	100	100	66.7	**91.7**	**4**
CoHex vs EDTA	100	100	75	100	**93.8**	**5**
CoHex vs M3	100	100	87.5	100	**96.9**	**6**

av: the average of the significant results

Order: evaluation from 1 to 6 (1: smallest different 6: biggest difference based on all parameters (pH+$CaCO_3$+KA+Clay)

Based on the average of the significance levels of all the pairwise analysis of the measurements along the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay). the least number of ‘not significant’ results belonged to EDTA and M3 pair, there has never been a significant difference between their results in the applied categories and the explanation force of significant difference is the weakest. So, even though the results of the statistical analysis of the overall, all-inclusive data proved that all the applied methods are statistically different, One-by-one analyses of the categories of the influencing factors resulted in different outcomes: there are ‘similarities’ not only differences. According to the first statistical pairwise analyses in the result chapter, all the methods differ, the most similar is the M3 and the EDTA methods but even between them, there was a significant difference. Furthermore, there is another pair that was not significantly different, taking into account that there was only one case where a significant difference occurred in the amount of Zn measured: CoHex and WA.

There was no significant difference between WA and EDTA but this pair formed a different group.

The next group where there was already a significant difference between the methods is WA and M3.

CoHex and EDTA followed the previous group in order, while the strongest difference is between CoHex and M3 and we can consider both as strong significance. These two pairs can be considered as a separate group.

Evaluating the differences based on all parameters the following order can be made (1 - smallest difference 6 - biggest difference):

1. **EDTA vs M3**
2. **CoHex vs WA**
3. **WA vs EDTA**
4. **WA vs M3**
5. **CoHex vs EDTA**
6. **CoHex vs M3**

EDTA vs MS were not significantly different from each other. The highest significant difference was between CoHex vs EDTA method.

5.5 Discussions concerning zinc measurements

Comparing the different analysis methods, the Mehlich 3 solution demonstrated a greater capacity of extraction of Zn in comparison to the other extractants, which is in agreement with other researchers like ABREU et al. (2002), PRADHAN et al. (2015). The acid reagents and chelating agents such as EDTA result in the higher extraction of Zn (VIDAL-VÁZQUEZ et al. 2005), which was also seen in the results of this study. The effect the pH, organic matter, clay content, Fe oxides, cation exchange capacity have on the soil properties has been discussed in several studies (JUNUS and COX 1987; SIMS and JOHNSON 1991; HADDAD and EVANS 1993; BORKERT et al. 1998), but there is less information about the effect of the chosen classification method in the evaluation of the zinc measurements. DIATTA and KOCIALKOWSKI (1998) reported that the adsorption of Zn by soils is influenced by the soil properties including the texture, calcium carbonate, and organic matter content. In a study conducted on soils with different textures for adsorption reactions of zinc, it is stated that light loam, silty medium loam, and silt loam soils having comparatively higher values for the adsorption maxima, bonding energy constant and differential buffering capacity of the soils will require higher rates of Zn to change in the solution concentration. In this study, the texture was firstly classified based on the Hungarian liquid limit according to Arany. Until the liquid limit according to Arany of 44, from a sandy loam to clayey loam texture, a strong correlation in the Zn measurements was shown between the M3 and EDTA method. We can summarise that not only the extraction method, but also some of the soil physicochemical properties and the chosen classification method affect the evaluation of the zinc measurements. From the comparison of the influencing factors, farmers can also gain extra knowledge where intervention is needed to use extra Zn for the proper fertilisation of their plants.

5.6 Conclusions concerning zinc measurements

Mehlich 3 solution demonstrated a greater capacity of extraction of Zn in comparison to the other extractants.

Zinc content measured by the six methods resulted in the following order: **CoHex < WA < EDTA < M3 < XRF.**

The relationship between EDTA and M3 Zn determination methods explains 71% variation ($R^2=0.71$ $p<0.001$), all the other determination coefficients are lower than 0.2 or aren't significant.

Evaluating the zinc contents according to two Arany-type texture categories based on the Hungarian advisory system showed that **in loam and clayey loam texture (38-50 KA), the measured zinc from the total was lower for all of the methods compared to the measurements in sandy loam texture.**

The linear relationship between the methods was much weaker in the case of loam/clayey loam soils.

In category of KA<38 EDTA and M3 methods of determining Zn have the highest determination coefficient explaining more than 84% of the total variation. EDTA vs WA relationship explains 67.3%, WA vs M3 50.6% and CoHex vs WA explains 47.4% of the total variance. In the category of KA 38-50 the determination coefficients between the pairs were smaller compared to the category of KA<38.

Based on the analyses of all data we can conclude that all methods are different. However, further analyses during the comparison of the methods based on the influencing factors, such as pH, lime content, texture class, and clay content proved that in some of the cases there are similarities among the methods and this way we can get more knowledge on the measurements and the results provided.

Based on the Pearson correlation analysis and the average of the significance levels of all the pairwise analyses of the measurements along the four influencing factors (pH (KCl), $CaCO_3$, Arany-type texture, and clay), it can be concluded that the least different methods for Zn determination are EDTA and M3 analyses methods.

Evaluating the differences based on all parameters the following order can be made (1 - smallest difference 6 - biggest difference):

1. **EDTA vs M3**
2. **CoHex vs WA**
3. **WA vs EDTA**
4. **WA vs M3**
5. **CoHex vs EDTA**
6. **CoHex vs M3**

We can summarize that **not only the extraction method but also some soil physicochemical properties and the chosen classification method affect the evaluation of zinc measurements.**

Based on these results, an important conclusion can be made: **analyzing all-inclusive data can result in very strong and significant differences**

between the applied method but it can be misleading as the in-depth analysis can prove otherwise.

6. Conclusions

In the first part of my thesis, I summarized the historical development of soil analysis methods in Hungary. This review aimed to provide a summary of the Hungarian soil examination methods, which has led to the actual soil testing procedures and interpretation. We can still learn a lot from past experiences and its reason-based good agricultural practices. What we can apply today and tomorrow in practice from the results of pedology, and in what direction we can start on the path of development, can only be perceived if we know the results of the past and take their guiding effects into account. Most of our methods today are rooted in the past, and we can judge and further develop the current situation of our field of science if we know the antecedents, the past. Our current soil testing system still provides usable results today, but following international trends, the domestic adoption of newer soil testing methods may provide new perspectives in the methodology of Hungarian soil testing. As we saw there are several methods used worldwide and the harmonization of methods, measurements and indicators for the sustainable management and protection of soil resources are increasingly important to comply with the tightening legislation and boundary conditions for sustainable agricultural production. In the harmonization procedure it is important to understand the background of our existing methods then to work out a methodology to compare the different methods and then harmonize the results.

The basic dataset of my thesis was seventy geo-referenced soil samples taken in Hungary, differing in soil typology, texture, and pH. These samples were analyzed with different extraction methods in the laboratory. I compared and evaluated the existing Hungarian soil analysis methods, AL, KCl, KCl-EDTA methods with Mehlich 3, Water, Cobalt Hexamine and XRF methods for phosphorus, magnesium and zinc measurements.

The novelty in the comparison is that the amount of P, Mg and Zn measured with different analysis methods were compared to the total contents measured with the XRF method. It was obvious, based on the data analysis that the XRF method measured significantly higher amounts, meaning a thousand times more than other methods.

Data were first compared for the whole dataset and then, in certain categories of $CaCO_3$-content, pH, liquid limit according to Arany and clay content.

It was proved that categorization of the influencing factors resulted in different correlation strengths than the analyses of the overall data, presuming that the increasing trend of clay, liquid limit according to “Arany” and lime content and the pH values were not proportional with the increase or decrease of the efficiency of the measurements.

The analyzed groups can also highlight where the correlation was strong, weak or none, shedding light on the range where the influencing magnitude was having significance.

Furthermore, a list of the compared measurement pairs is provided, based on the number of significant differences calculated in all of the analyzed categories of the influencing factors

Based on these results, it was concluded that analyzing all-inclusive data can result in very strong and significant differences between the applied methods. But it can be misleading as the in-depth analysis can prove otherwise.

Comparison of the methods based on the influencing factors proved that in some of the cases there are similarities among the methods and this way we can get more knowledge on the measurements and the results provided.

The results also guide some possible categories where measurements can provide a new way of forming the categories of e.g. available zinc based on lime content, or clay content or pH, etc. As a result, we can gain extra knowledge from the comparison of the influencing factors to know where intervention is needed to use extra P, Mg Zn for the proper fertilization. This possibility of the new targeted measurements, however, is out of the scope of this study.

Despite traditional soil, tests are available in huge numbers, with learning more about soils analysis methods and their interpretations, could lead to a new dimension in the Hungarian soil science.

In conclusion not only the well-known extraction methods and the soil but also the chosen classification method of the properties and also, the statistical analysis (measuring all data or certain classes) affect the evaluation of P, Mg, Zn measurements. This comparative analysis study can provide a guide to interpret the different analysis methods on the way of harmonization.

7. Theses

1. It was proved that not only the extraction methods but also the chosen classification of the influencing soil parameters and the statistical analysis (measuring all data or certain classes) affected the evaluation of the results of soil phosphorus, magnesium and zinc measurements.

2. The orders of magnitude of the extraction efficiency of phosphorus, magnesium and zinc measurements are determined based on evaluating the following methods: WA – water extraction, KCl – potassium chloride, KCl-EDTA – potassium chloride ethylenediaminetetraacetic acid, AL – ammonium lactate, M3 – Mehlich 3, CoHex – cobalt hexamine, XRF – X-ray fluorescence.

   Based on the results, the **phosphorus** content measured by the six methods resulted in the following order of measured magnitude:
   P-WA< CoHex < P-WA(PO_4) < M3 < AL < XRF

   Based on the results, the **magnesium** content measured by the six methods resulted in the following order of measured magnitude:
   WA < KCl < CoHex < M3 < XRF

   Based on the results, **zinc** content measured by the six methods resulted in the following order of measured magnitude:
   CoHex < WA < EDTA < M3 < XRF

3. Evaluating the differences in P determination methods based on all parameters the following order can be made:
    1. P-WA(PO_4) vs P-WA, P-WA vs CoHex
    2. P-WA(PO_4) vs CoHex
    3. AL vs M3
    4. CoHex vs AL
    5. CoHex vs M3
    6. P-WA(PO_4) vs AL
    7. P-WA(PO_4) vs M3, P-WA(PO_4) vs M3
    8. P-WA vs AL

Evaluating the differences in **Mg** determination methods based on all parameters the following order can be made:

1. M3 vs CoHex
2. M3 vs KCl
3. CoHex vs KCl
4. WA vs CoHex
5. WA vs KCl
6. WA vs M3

Evaluating the differences in **Zn** determination methods based on all parameters the following order can be made:

1. EDTA vs M3
2. CoHex vs WA
3. WA vs EDTA
4. WA vs M3
5. CoHex vs EDTA
6. CoHex vs M3

4. The linear relationship between P content determined by P-WA and M3 methods was significant with the determination coefficients of 0.72 for P-WA(PO_4) versus M3 and 0.67 for P-WA versus M3.

5. Comparing the results of AL-phosphorus method with the results of P-WA(PO_4), P-WA , CoHex and M3 methods in lime free – low lime content soils ($CaCO_3$ w/w % < 1), showed weak significant linear relationships explaining at 39–57% variance ($0.39 \leq R^2 \leq 0.57$). In the category of higher lime content soils ($CaCO_3$ w/w % >1) the only significant relationship was determined between CoHex versus AL (p=0.02) explaining 20% of the variance.

6. The linear relationship between KCl and CoHex methods had the highest significant determination coefficient, (R^2=0.96 p<0.001) then followed by WA versus M3 (R^2=0.68, p<0.001), M3 versus CoHex (R^2=0.66, p<0.001) and M3 versus KCl (R^2=0.60, p<0.001).

7. In all lime categories the linear relationship between CoHex versus KCl methods was significant, explaining more than 95% variance (R^2>0.95 p<0.001).

   The higher $CaCO_3$-content ($CaCO_3$ w/w % > 0.1) showed a lower determination coefficient in case of M3 versus CoHex and M3 versus KCl methods.
   The results of WA vs M3, WA vs CoHex and WA vs KCl pairs showed opposite results; in lime free soils there was no significant relationship between these methods, but the higher lime ($CaCO_3$ w/w % > 0.1) content resulted in a significant linear relationship and higher determination coefficient.

8. The linear relationship between Zn content determined by KCl-EDTA and M3 methods is significant, with 0.71 determination coefficient (R^2=0.71, p<0.001).

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INTERNET LINKS:

1. http://www.fao.org/global-soil-partnership/glosolan/en/
2. http://www.fao.org/global-soil-partnership/en/

Annexes

Annex 1: Basic data; soil moisture state, land use, land cover, landscape position, slope, and soil erosion data at each sampling location

Nr	Barcode	Soil Moisture	Landuse	Landcover	Landscape position	Slope %	soil erosion
1	1HUA1005 60A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
2	1HUA1005 46A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
3	1HUA1005 12A17	humid	Arable Land	Cultivated Land (covered By Plants)	Slope	2	No
4	1HUA1005 09A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
5	1HUA1005 61A17	dry	ArableLand	Cultivated Land (covered By Plants)	Flat Area	0	No
6	1HUA1005 48A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
7	1HUA1005 14A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
8	1HUA1005 11A17	humid	Grazing Land	Cultivated Land (covered By Plants)	Flat Area	0	No
9	1HUA1005 44A17	dry	Horticultural Land	Cultivated Land (covered By Plants)	Slope	4	Mild
10	1HUA1005 41A17	dry	Forest	Closed Forest	Slope	3	No
11	1HUA1005 47A17	dry	Arable Land	CultivatedLand (covered By Plants)	Flat Area	0	No
12	1HUA1005 17A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
13	1HUA1005 10A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
14	1HUA1005 21A17	humid	Arable Land	Cultivated Land (covered By Plants)	Top Of Hilll	1	No
15	1HUA1005 19A17	dry	Arable Land	Cultivated Land (covered By Plants)	FlatArea	0	No
16	1HUA1005 20A17	dry	Arable Land	Cultivated Land (covered By Plants)	FlatArea	0	No
17	1HUA1005 30A17	dry	Arable Land	Cultivated Land (covered By Plants)	Slope	10	Mild
18	1HUA1005 22A17	humid	Arable Land	Cultivated Land (covered By Plants)	Top Of Hilll	0	No
19	1HUA1005 31A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
20	1HUA1005 15A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
21	1HUA1005 25A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
22	1HUA1005 43A17	dry	Arable Land	CultivatedLand (Fallow)	Slope	11	No
23	1HUA1005 02A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
24	1HUA1005 26A17	dry	Forest	Closed Forest	Flat Area	0	No
25	1HUA1005 24A17	humid	Arable Land	Cultivated Land (covered By Plants)	Slope	4	Mild

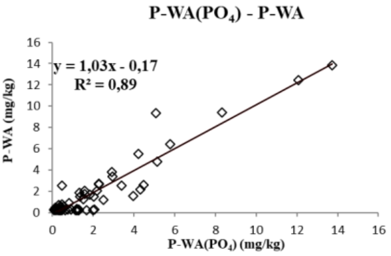
Annex 1: Basic data; soil moisture state, land use, land cover, landscape position, slope, and soil erosion data at each sampling location

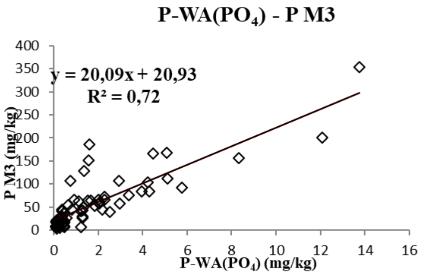
Nr	Barcode	Soil Moisture	Landuse	Landcover	Landscape position	Slope	soil erosion
26	1HUA100527A17	dry	Arable Land	Cultivated Land (Fallow)	Slope	2	No
27	1HUA100545A17	dry	Grazing Land	Cultivated Land (covered By Plants)	Slope	3	No
28	1HUA100516A17	dry	Grazing Land	Open Forest	Slope	9	Mild
29	1HUA100523A17	humid	Arable Land	Cultivated Land (covered By Plants)	Top Of Hilll	0	No
30	1HUA100501A17	humid	Forest	Open Forest	Slope	5	No
31	1HUA100503A17	dry	Arable Land	Cultivated Land (covered By Plants)	Slope	2	No
32	1HUA100529A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
33	1HUA100528A17	dry	Arable Land	Cultivated Land (covered By Plants)	Slope	5	Mild
34	1HUA100569A17	wet	Arable Land	Cultivated Land (covered By Plants)	Slope	4	No
35	1HUA100607A17	dry	Arable Land	Cultivated Land (covered By Plants)	Slope	4	No
36	1HUA100625A17	dry	Arable Land	Cultivated Land (Fallow)	Top Of Hilll	3	No
37	1HUA100533A17	humid	Forest	ClosedForest	Flat Area	0	No
38	1HUA100551A17	humid	Grazing Land	SparseForest	Slope	4	No
39	1HUA100508A17	humid	Arable Land	Cultivated Land (covered By Plants)	Depression	0	No
40	1HUA100506A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
41	1HUA100507A17	humid	Arable Land	Cultivated Land (Fallow)	Flat Area	0	No
42	1HUA100604A17	wet	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
43	1HUA100567A17	dry	Arable Land	Cultivated Land (Fallow)	Flat Area	0	No
44	1HUA100603A17	wet	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
45	1HUA100549A17	dry	Arable Land	Cultivated Land (Fallow)	Flat Area	0	No
46	1HUA100619A17	dry	Forest	Closed Forest	Slope	5	No
47	1HUA100614A17	dry	Arable Land	Cultivated Land (Fallow)	Flat Area	0	No
48	1HUA100626A17	dry	Arable Land	Cultivated Land (Fallow)	Flat Area	2	No
49	1HUA100620A17	dry	Arable Land	Cultivated Land (Fallow)	Slope	4	No
50	1HUA100553A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No

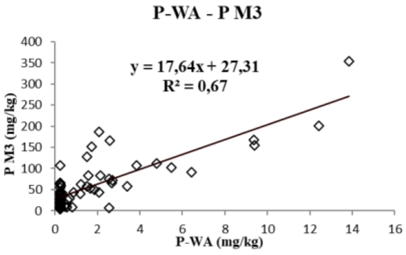
Annex 1: Basic data; soil moisture state, land use, land cover, landscape position, slope, and soil erosion data at each sampling location

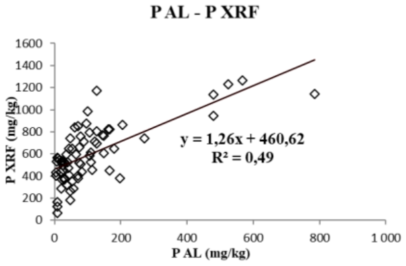
Nr	Barcode	Soil Moisture	Landuse	Landcover	Landscape position	Slope	soil erosion
51	1HUA100554A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
52	1HUA100552A17	humid	Arable Land	Cultivated Land (Fallow)	Flat Area	0	No
53	1HUA100605A17	wet	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
54	1HUA100297A17	dry	Arable Land	Cultivated Land (Fallow)	Flat Area	1	No
55	1HUA100601A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
56	1HUA100538A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
57	1HUA100536A17	dry	Grazing Land	Cultivated Land (covered By Plants)	Flat Area	0	No
58	1HUA100537A17	dry	Arable Land	Cultivated Land (covered By Plants)	Slope	3	No
59	1HUA100550A17	humid	Arable Land	Cultivated Land (Fallow)	Slope	2	No
60	1HUA100608A17	dry	Arable Land	Cultivated Land (Fallow)	FlatArea	0	No
61	1HUA100610A17	dry	Arable Land	Cultivated Land (Fallow)	Top Of Hilll	3	No
62	1HUA100563A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
63	1HUA100566A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
64	1HUA100606A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
65	1HUA100532A17	humid	Arable Land	Cultivated Land (covered By Plants)	Flat Area	1	No
66	1HUA100564A17	dry	Arable Land	Cultivated Land (Fallow)	Flat Area	0	No
67	1HUA100534A17	humid	Arable Land	Cultivated Land (covered By Plants)	Slope	2	No
68	1HUA100565A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No
69	1HUA100562A17	dry	Arable Land	Cultivated Land (covered By Plants)	Flat Area	1	No
70	1HUA100602A17	wet	Arable Land	Cultivated Land (covered By Plants)	Flat Area	0	No

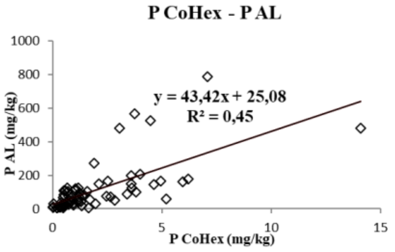
Annex 2: The results of the correlation regression analysis between the P contents measured by P-WA, P-WA(PO_4), M3, CoHex, AL, XRF methods.

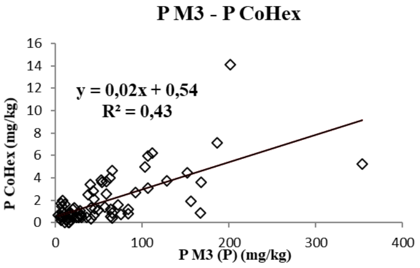


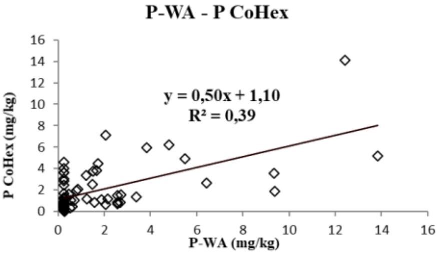


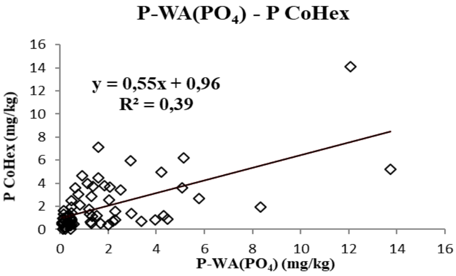


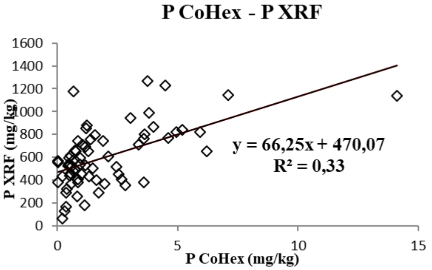


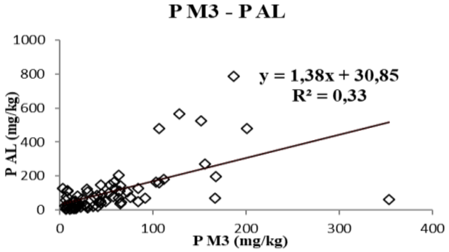


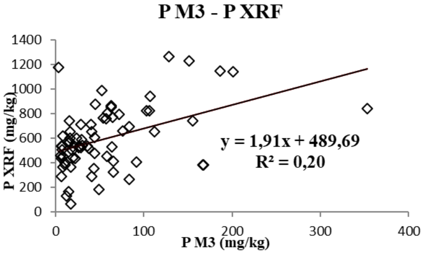


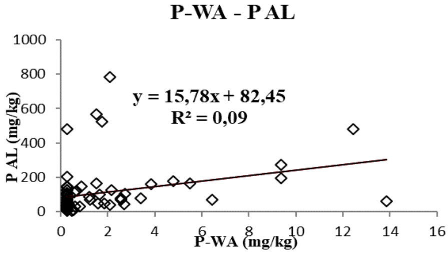

P-WA - P CoHex
y = 0,50x + 1,10
R² = 0,39
P CoHex (mg/kg)
P-WA (mg/kg)
0
2
4
6
8
10
12
14
16

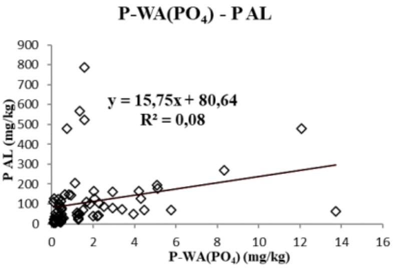

P-WA(PO4) - P CoHex
y = 0,55x + 0,96
R² = 0,39
P CoHex (mg/kg)
P-WA(PO4) (mg/kg)
0
2
4
6
8
10
12
14
16

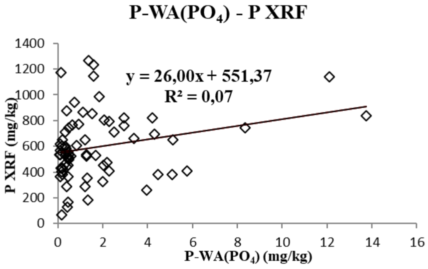

P CoHex - P XRF
y = 66,25x + 470,07
R² = 0,33
P XRF (mg/kg)
P CoHex (mg/kg)
0
200
400
600
800
1000
1200
1400
1600
5
10
15

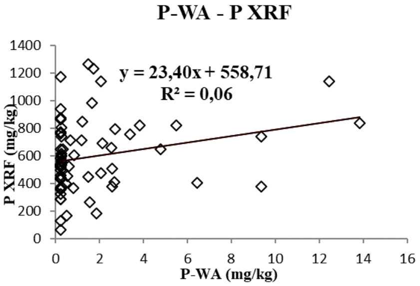

P M3 - P AL
y = 1,38x + 30,85
R² = 0,33
P AL (mg/kg)
P M3 (mg/kg)
0
200
400
600
800
1000
100
300


P M3 - P XRF
y = 1,91x + 489,69
R² = 0,20
P XRF (mg/kg)
P M3 (mg/kg)
0
200
400
600
800
1000
1200
1400
100
300

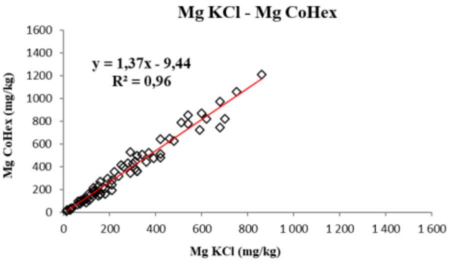

P-WA - P AL
y = 15,78x + 82,45
R² = 0,09
P AL (mg/kg)
P-WA (mg/kg)
0
200
400
600
800
1000
2
4
6
8
10
12
14
16

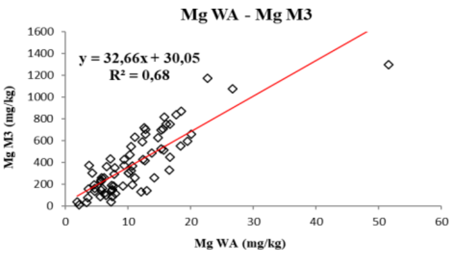

P-WA(PO4) - P AL
y = 15,75x + 80,64
R² = 0,08
P AL (mg/kg)
900
800
700
600
500
400
300
200
100
0
0
2
4
6
8
10
12
14
16
P-WA(PO4) (mg/kg)

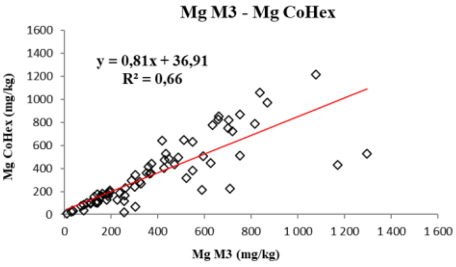

P-WA(PO4) - P XRF
y = 26,00x + 551,37
R² = 0,07
P XRF (mg/kg)
1400
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
16
P-WA(PO4) (mg/kg)

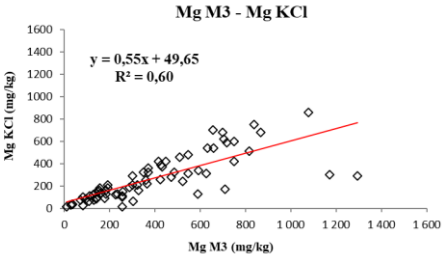

P-WA - P XRF
y = 23,40x + 558,71
R² = 0,06
P XRF (mg/kg)
1400
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
16
P-WA (mg/kg)

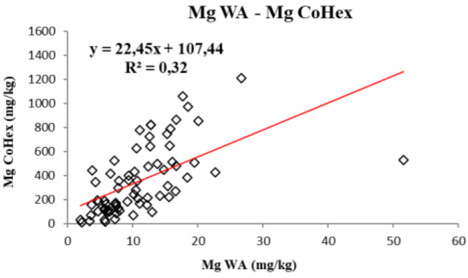
Annex 3: The results of the correlation regression analysis between the P contents measured by WA, M3, CoHex, KCl, XRF methods.

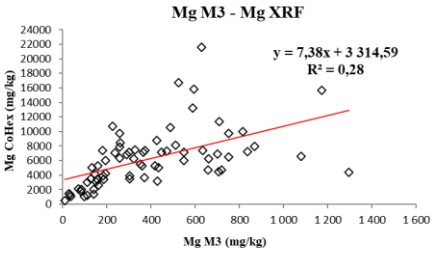


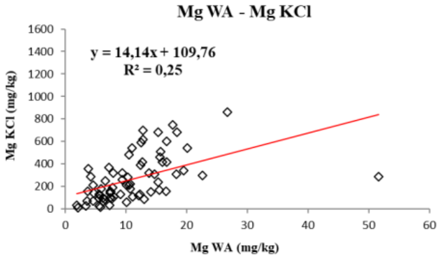


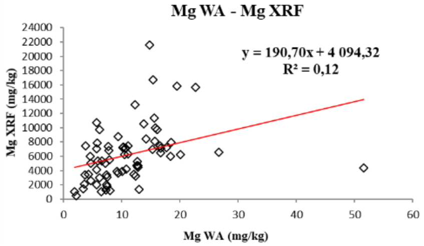


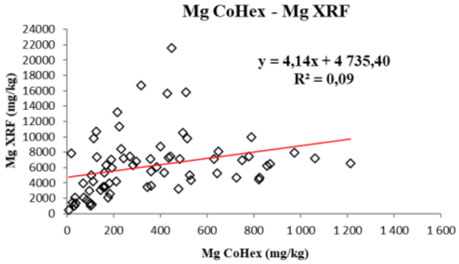


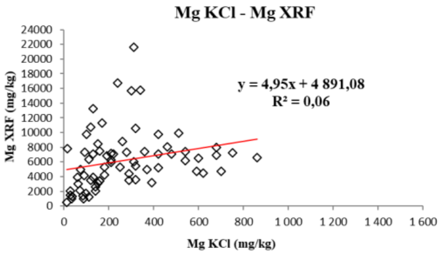




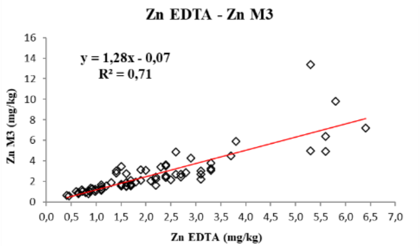

Mg WA - Mg KCl

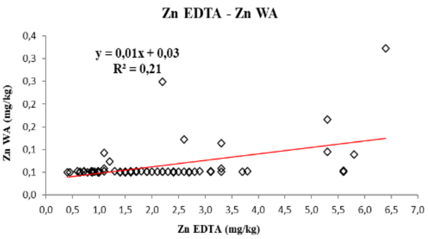

Mg WA - Mg XRF

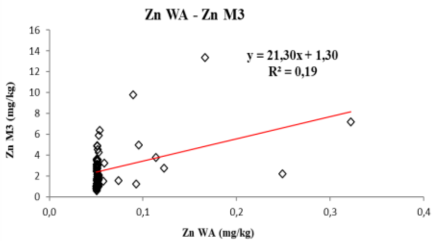

Mg CoHex - Mg XRF

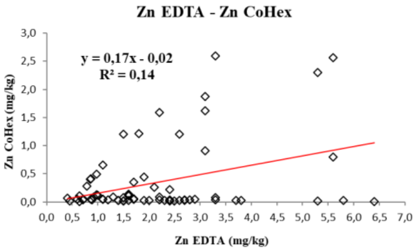

Mg KCl - Mg XRF

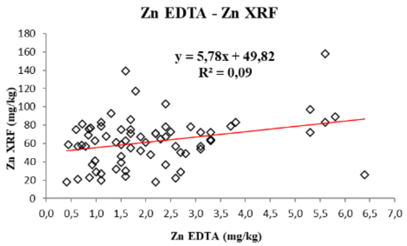
Annex 4. The results of the correlation regression analysis between the Zn contents measured by WA, M3, CoHex, EDTA, XRF methods.

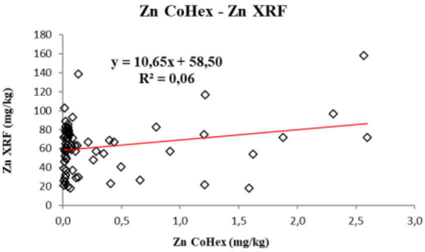


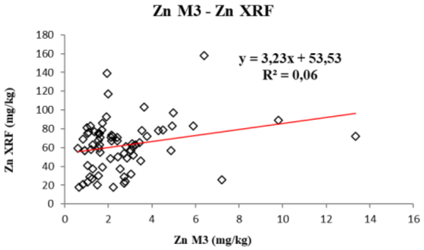


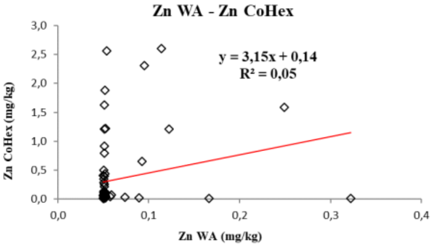


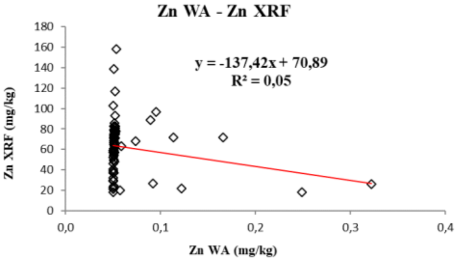


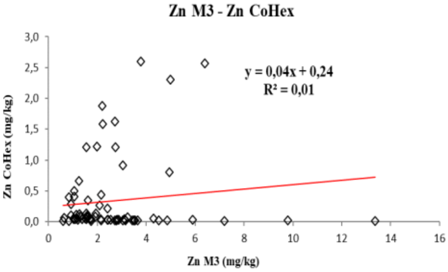





Zn M3 - Zn XRF
y = 3,23x + 53,53
R² = 0,06
Zn XRF (mg/kg)
180
160
140
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
Zn M3 (mg/kg)


Zn WA - Zn CoHex
y = 3,15x + 0,14
R² = 0,05
Zn CoHex (mg/kg)
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0,0
0,1
0,2
0,3
0,4
Zn WA (mg/kg)


Zn WA - Zn XRF
y = -137,42x + 70,89
R² = 0,05
Zn XRF (mg/kg)
180
160
140
120
100
80
60
40
20
0
0,0
0,1
0,2
0,3
0,4
Zn WA (mg/kg)


Zn M3 - Zn CoHex
y = 0,04x + 0,24
R² = 0,01
Zn CoHex (mg/kg)
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
2
4
6
8
10
12
14
16
Zn M3 (mg/kg)