OFFICIAL FACULTY OF AGRONOMIC SCIENCES AT GEMBLOUX (BELGIUM)

PHOSPHORUS IN SOME SOILS OF THE PROVINCE OF SARAGOSSA (SPAIN)

Disertation to obtain the pH degree in Agricultural Sciences

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I N D E X

Pag.

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

LITERATURE REVISED

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CHAPTER 1

1.1. INTRODUCTION

1.2. GENERAL VIEW OF SOIL PHOSPHORUS

1.1. INTRODUCTION

The province of Saragossa situated in the midle of the Ebro Valley - shows the visitor a panorama proper to a semi-arid region where soil forming factors such as temperature rainfall, parent material, vegetation, - topography have been conjugated in order to produce soils such as:

- Serosems (dominant in the province)
- Brown soils (in small areas)
- Soils on tenaces and secondary soils on gravel (lehm pardo)
- Alluvial meadow soils (naturaly calcareous).

The dominant soils in this province, like those belonging to the semi-arid regions show problems related to the phosphorus, in which the chemistry of this element in calcareous soils is involved. This chemistry includes nature, reactions among soil constituents, soil phosphorus forms - with the phosphorus added through dressings, and as well, the dynamics - that this element exhibits in its transfer to the soil solution and its - later absorption by crops.

On the other hand, we found that the Saragossa province has 90,77 % of this total surface cultivated its distribution being 82,12 % under dry farming (with crops such as cereals, vineyards and olives) and 17,8 % under irrigation (with crops such as fruit-trees, vegetables, alfalfa and - maize). These types of agriculture are respectively localized on serosem soils and brown soils for dry farming, and alluvial meadow soils, soil developed on terraces and small areas of serosem are irrigated.

In this study no attempt is made to give norms for phosphorus fertilization for different crops and soils, it being and initial study in order to get information as to the situation of the phosphorus in the principal soils of this province. In this way, we shall later on be able, with suitable trials concerned with fertilizers, form and epochs of application, management, etc., to establish an appropriate policy regarding the use of fertilizers in these soils.

In order to achieve the above mentioned knowledge, we have believed that the characterization of gypsum serosem, marly serosem, soil developed on terraces, alluvial meadow soil and brown soil in relation to:

1) Phosphorus distribution along soil profile

This part includes:

A) Total P organic and inorganic in soil horizons.

B) The fractions that form this soil inorganic phosphorus.

C) Phosphorus compounds in the predominant soil inorganic phosphorus fraction.

In this way, we whall be able to have a real picture of phosphorus in the soil phase.

2) Physicochemical processes

This part has the purpose of knowing what the behaviour is like of these soils related to:

A) Adsorption.- By the use of the Langmuir isotherm one will obtain the maximum Phosphorus adsorption and, as well, the energy constant with which it is united to the soil.

In general the literature cites two laboratory procedures that are used for the evaluation of this process: diluted potassium diphosphate solutions buffered at pH 7,0 and the other method consiste of: increased amounts of calcium diphosphate in a medium 0.01 M of calcium chloride solution.

This is the first time that a study concerned with phosphorus adsorption by these soils has been carried out; for that reason, we have believed that it would be more reasonable to carry out an evaluation of this process through both laboratory methods.

B) Desorption.- We have used two laboratory methods; one of them was on the basis of 14 water extractions in order to see the mechanism of this phosphorus desorption, and the other procedure consisted of an anion resin for the performance of this P desorption according to time.

C) Transfer of the phosphorus adsorbed by soil.- In this part we try to reflect what the transfer of the phosphorus adsorbed by these soils has been like, after an initial 8 p.p.m. phosphorus addition.

This initial phosphorus concentration corresponds to the I area of P adsorption in these soils and, therefore, we believe that it can furnish a real picture of the soil conditions.

3) Dynamics of soil phosphorus and crop growth

We have mentioned before that our purpose is to characterize these soils in relation to their phosphorus status, therefore, in this part, it is logical to verify under normal soil conditions (no P fertilizer applied) if the ray-grass grown in these soils shows a similar or a different yield. If we obtain significant differences in dry matter or phosphorus yields, we shall try to explain these differences through:

A) What was the contribution of soil inorganic phosphorus fractions to the P absorbed by these plants.

B) Through the evaluation of the phosphorus assimilable by the plant, obtained by three quick laboratory assessments.

C) C) How the factors of fertility of the soil have intervened in the regulation of this supply of phosphorus to the plant.

In order to localise our own study in the broad field of researchs on soil phosphorus it seems better to us to review briefly the literature on this subject.

1.2. GENERAL VIEW OF SOIL PHOSPHORUS

Apatite is an accessory mineral in rocks; it constitutes 95 % of the phosphorus minerals that exist in the earth's crust. Its content in soil is about 0.12 %, being, for this reason, a microcomponent of soils.

According to Pettijohn 1.966 (129) a main feature of apatite is its persistence in the rocks; in fact, in the sediments from the Archaic Era to the Pleistocen Period it is easily found as such, while in the soil it is transformed in secondary minerals. Thus, when a rock is subjected to changes in temperature, these produce distensions and contractions in the rock and, as a consequence, its breaking unto fragments, and by friction they are crushed into particles. During this friction process, the sides of the apatite will be rounded off, in this way making it lose its initial shape and then it will become more suitable for the latter transformations.

Apatite is attacked by soil microorganisms through their segregation of organic acids such as: oxalic, glycolic, citric, etc., that provoke the solubilization of the phosphorus of this mineral due to the chelating effect of these organic acids on the calcium ion.

There are several soil microorganisms that act on apatite; thus we have bacteria (Bacillus meghaterium fosfaticum): a part of the phosphorus solubilized by them is incorporated in their organism, and in this way apatite was transformed into organic phosphorus; another amount of this phosphorus solubilized by these bacteria is used by other soil microorganisms, for example: this phosphorus contributes towards the azotobacten being able to perform its functions of Nitrogen fixation. On the other hand, fungi influence this solubilization of the phosphorus of this mineral and these soil microorganisms are responsible for the organic phosphorus found in soils, even in the deepest soil horizons.

On the other hand, phosphorus has an ionic radium of 0.35 A similar to that of silicon (0.42 Aº), these elements entering inside a tetahedral configuration; however, that of the phosphorus has the peculiarity of showing unions with Cl^-, F^-, OH^-, $CO2^=$ as anions, while that of silicon offers unions with other silicon tetrahedrons or aluminum, magnesium and iron octahedrons.

For this reason, we can admit that in apatite there exists a series of compounds such as: fluor-apatite, chloroapatite, hydroxy-apatite, carbonate apatite.

Basset 1.919 (14) asserts that is pure systems the hydroxy-apatite was the most stable from under an ample range of acidity and for that reason Basset concluds that this form will be the only form of calcium phosphate that exists under normal soil conditions; however, for Black 1.967 (20) it is fluor-apatite.

In light weathered soils, apatite is present in both coarser and finer textural fractions with similar contents, (Shipp and Matelsky 1.960 (142)), and in moderate weathered soils apatite is found in sand and silt fractions and in older soils it can be absent (Williams and Walker 1.967 (169)).

Total phosphorus content in the arable layer is 0.062 % in the U.S.A. (Lipman and Coneybeare 1.936 (20)); 0.06-0.10 % in Finland (Kaila 1.963 (86)); and 0.06-0.308 % in Australian soils (Wild A. 1.958 (171)).

Several soil workers (Allaway and Rhoades, 1.951 (31)); Bates and - Baker 1.960 (15); Godfrey and Curtis 1.954 (62); Kaila 1.963 (87); Walker and Adams 1.959 (166) have found that the total phosphorus distribution along the soil profile in soils developed from the same parent material, shows the next sequence: C horizon A horizon B horizon.

Total phosphorus is formed by organic and inorganic fractions, the former are included in the organic matter of the soil and then their distribution along the soil profile will be similar to that shown for the - soil organic matter.

At present, only three compounds that constitute the organic phosphorus have been identified: nucleic acid (1-3 %) phospholipid (2 %) and hexaphosphate inositol (35 %). This total organic phosphorus is not a stable form under soil conditions because it is subjected to a mineralization process produced by the soil microorganisms through an enzymatic action.

This mineralization of organic phosphorus can be justified by:

1) The fact that there have been found notable differences among - the organic phosphorus contents in cultivated and virgin lands; moreover, if these lands are put under conditions of cultivation, a pronounced lowering in this organic phosphorus content is observed in a few years.

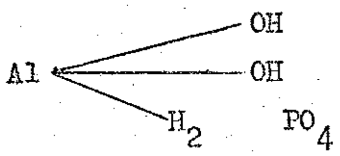
2) By inclubation of soil samples carried out under suitable conditions of temperature and humidity in laboratory tests. After a short time of inclubation, an increase in phosphorus extracted by acid was found and this amount corresponded to the decrease of organic phosphorus content.

3) By an association with other soil properties: it has been verified that the amount of organic phosphorus in several soils has been well correlated with those of organic carbon and nitrogen, and the rate of organic phosphorus mineralization was of the same magnitude as those of organic carbon and nitrogen.

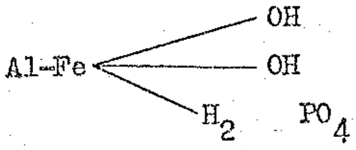
Although in some cases, a slight change of soil pH produced by liming could influence the rate of organic phosphorus mineralization more than those of carbon and nitrogen (Thompson, Black and Zoellner 1.954 - (159)).

The soil inorganic phosphorus includes several compounds that have been identified by their mineralogical, physical and chemical features. So, Shipp and Maltesky 1.960 (142) have recognized apatite in sand and - silt fractions; according to mineralogical procedures. Other soil workers have used laboratory procedures based upon the criterion of solubility.

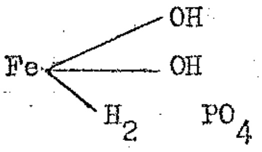
On the other hand, we know that when weathering proceeds in soil, - acidity is developed an the apatite tends to disappear and the phosphorus solubilized from this mineral tends to unite itself to the aluminium and iron ions coming from the silicate minerals. These unions are ionic exchangeable reactions in which the PO4 replaces the OH^{-} or O from these oxides hydroxides minerals; producing compounds such as:



Variscite



Banendite



Strenghite

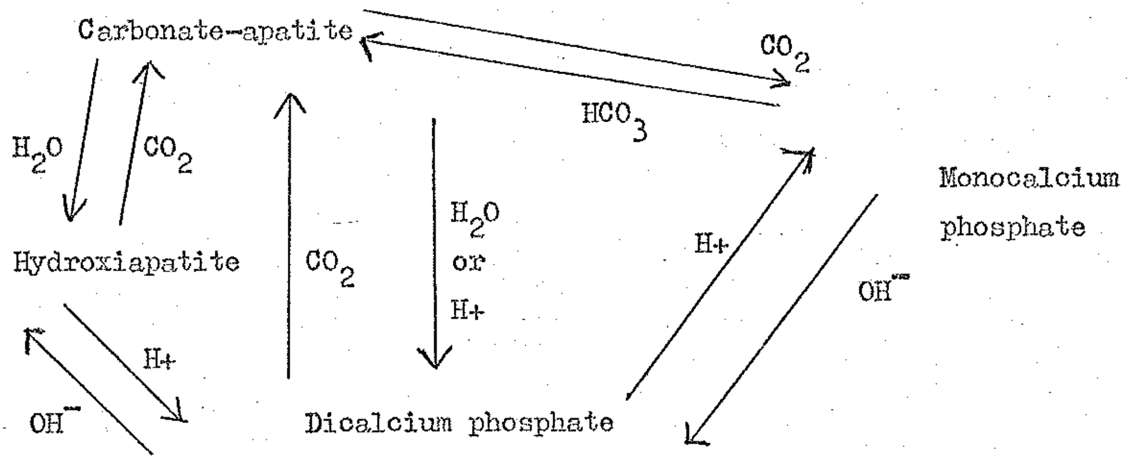
These above compounds by combination with K, NH_4 and Mg can produce crystalized forms such as: Mynuirite, Tarankite and Wavellite.

Under impeded drainage conditions in a soil or reduction conditions provoked by certain crops (rice), in acid soils there can exist a vivianite (fe_3 (PO_4) H_2O), easily soluble, and for that it contributes to the phosphorus absorbed by rice.

In older soils, the weathering process has been so strong that the phosphorus predominantes, occluded by the free iron oxides-hydroxides, this form of phosphorus showing similar properties to those of the dufrenite (Fe_3 (OH_3) PO_4) in the Fe 0 OH solution.

In calcareous soils, where the weathering has been slight, the dominant phosphorus form is a carbonate-apatite (M.G. George and Breazeale - 1.931 (114)) and the compounds of calcium phosphate are governed by the presence of free calcium ion that comes from the lime and gypsum of these soils.

The above situation can be summarized in the following diagram: (L.T. Kardos 1.967 (89)).

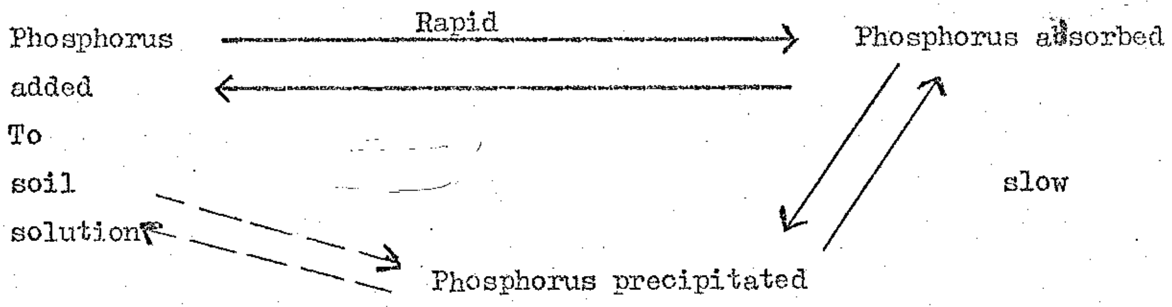


Octocalcium phosphate was not included because it is considered an unstable from in the soil.

From the above diagram, it can be deduced that the soil pH influences the phosphorus compound that predominates and at the same time the nature of these calcium phosphate compounds due to the amount and presence of free calcium ion.

PHYSICO-CHEMICAL PROCESSES BETWEEN PHOSPHORUS AND SOIL

Soil is such a - heterogeneous and dynamic medium and phosphorus is, perse, such an active element that their interaction gives a mechanism - such as:



(O. Talibudeen 1.973 (152)).

From this scheme it can be deduced:

1) That there exists a quick reaction in which phosphorus is adsorbed by soil constituents and perhaps by soil phosphorus compounds.

2) A slower reaction is produced in which the phosphorus is incorporated in some soil constituents and as a consequence a new formation of phosphorus compounds occurs.

Normally, adsorption is known as the concentration of liquid or gas on the surface of a solid and its incorporation inside the solid is denominated absorption.

In soils, the elimination of phosphorus from the soil solution is due to both processes and it receives a collective name of sorption of phosphorus by the soil.

Phosphorus adsorption in the soil is closely related to the surface area exhibited by the different soil constituents and those of soil phosphorus forms. In order to get information about the mechanisms by which this phosphorus adsorption by soil is produced, several soil workers (Boichot et al. 1.950 (26); Bolt 1.968 (27); Cole C.V. and Olsen 1.953 (37); Cole C.V. and Olsen S.R. 1.959 (38); Haan F.A.M. 1.966 (69); Muljadi D. et al. 1.966 (116, 117) have studied this process with clays (Kaolinite, Montmotillonite, etc.), aluminium and iron oxides-hydroxides and calcium carbonate.

From these studies, they can develop some theories about the mechanism of phosphorus adsorption by acid and calcareous soils.

In calcareous soils, where exist calcium carbonate, soluble salts and, naturally, clay (montmotillonite, illite, clorite, vermiculite, etc.) satured by calcium, the mechanism of phosphorus adsorption is a combination of the individual reactions had for the phosphorus with calcium carbonate and with calcium clays.

The theories which try to explain the process of phosphorus adsorptions, for both these soil constituents, are as follows:

1) Boichot et al. 1.950 (26) were the pioneers in the study of the reaction of diluted phosphorus solutions with calcium carbonate. They found that there existed an initial phosphorus adsorption by calcium carbonate and this amount of phosphorus adsorbed was closely related to the size of calcium carbonate particles. This fact was well defined by Cole and Olsen in 1.954 (38) through a study of phosphorus diluted solutions, P^{32} and calcium carbonate. These authors concluted that, in fact, for a 2×10^{-4} M P concentration in final solution the phosphorus adsorption by calcium carbonate was produced and it was like a monomolecular layer of phosphorus surrounding these particles due to the fact that these adsorption values followed the Langmuir isotherm in this phosphorus concentration range in final solution. At concentrations higher than 2×10^{-4} M P in the final solution, this monomolecular phosphorus layer thickens and it starts the formation of a nucleus of calcium phosphate crystalization until the process ends with a precipitation of calcium phosphate on the surface of the calcium carbonate.

2) For calcium clays, at the beginning the phosphorus seems to be adsorbed as a monomolecular layer or situated in an ionic atmosphere surrounding these clays, after that this phosphorus reacts with the exchangeable calcium of these clays in order to form a nucleus of dicalcium phosphate crystalization, and can be precipitated as a separate phase or can be readsorbed on the surface of the calcium clays (Russell 1.950 (138)).

In acid soils, phosphorus adsorption has been explained through theories concerned with the displacement of OH^- from the borders of the clay structure or by the phosphorus neutralization of the positive charges in these sides of the clay structure (Bolt 1.968 (27; Haan F.A.M. 1.966 (69); Muljadi D. et al. (116, 117); Wey R. 1.956 (170)).

Phosphorus adsorbed by soil is an immediate form of phosphorus supply to the soil solution while the forms of phosphorus precipitated can be considered as being of slow action as their passing to the solution will depend on the solubility which they present.

This solubility is governed by the ionic activities in the soil solution. In this way, calcium phosphate compounds in soils that show a high pH value reflect low solubility and therefore these phosphorus compounds are not assimilable by the plant while iron and aluminium phosphates in acid soils are not soluble, however the liming of these soils produces an increase in the solubility of these phosphorus factions due to the decreasing of the activity in the aluminium and iron ions.

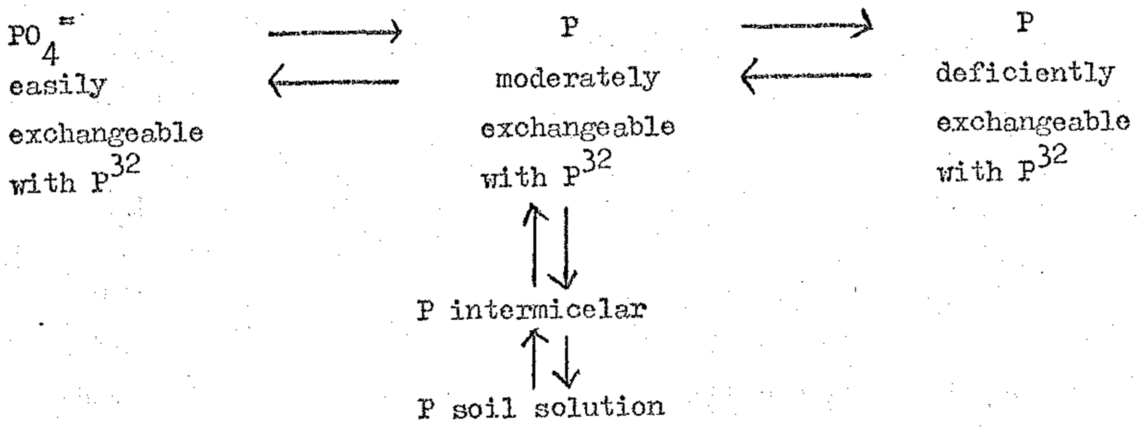
The phosphorus transfer from the solid phase to the soil solution is known as phosphorus desorption, this process being described as an hydrolytic displacement reaction (if this reaction occurs in water). This reaction was represented by Shapiro and Fried 1.959 (140) by the following equation:

$$\text{Soil P} \quad \underset{K_2 - \text{Soil OH}}{\overset{K_1 \times OH^-}{\rightleftarrows}} \quad \text{P solution}$$

In which the soil - P is in equilibrium with the P solution.

This phosphorus desorption in relation to time has been evaluated by several laboratory procedures: water leaching of soil samples (Fried M. and Shapiro R.E. 1.956 (53)); by a-nion resin method (Amer et al. 1.955 (4)) and by an isotopic dilution method (Talibudeen O. 1.957 (151)).

All these procedures have shown the existence of the different reactions that take place in this phosphorus desorption and at the same time that there exist several phosphorus forms that can intervene and which are as follows: (O. Talibudeen 1.957 (156)).



According to O. Talibudeen:

1) The PO_4 easily exchangeable with P^{32} is equal to: P adsorbed, P fixed in external surface of minerals and macropores, organic P labile.

2) The PO_4 moderately exchangeable with P^{32} is equal to: Sorbed chemical phosphorus, P fixe in internal surfaces and micropores, Organic - phosphorus, moderately exchangeable.

3) The PO_4 slowly exchangeable with P^{32} is equal to: apatite crystalized on surface layers and stable organic phosphorus.

From the above scheme we can deduce that there exists a situation - of equilibrium among the different forms of labile phosphorus in the solid phase of the soil that will intervene in the quick, moderate and slow reactions of phosphorus desorption in relation to time.

SITUATION OF PHOSPHORUS IN SOIL FERTILITY

According to E.G. Williams 1.963 (173), the yields and phosphorus - content in crops is an expression of the phosphorus status, combined with the capacity of a soil to transfer it, physiological features of the - - plants and effects of other soil factors such as: pH, humidity, aireation, microbial activity, equilibrium and transfer of other nutrients that con trol plant growth and govern, directly or indirectly, the phosphorus absorption by plants.

An evaluating procedure for the status of a nutrient (M) in soil must take into account phases:

$$\begin{array}{ccccccc} M & \longrightarrow & M & \longrightarrow & M & \longrightarrow & M \\ \text{Solid} & & \text{Solid} & & \text{in} & & \text{in} \\ \text{phase} & & \text{solution} & & \text{neighbourhood} & & \text{plant} \\ & & & & \text{roots} & & \end{array}$$

In order to evaluate this situation, it is necessary to use chemical and biological procedures. Different soil workers, making, use of the correlation procedures between plant yields and soil phosphorus extracted by laboratory methods, have tried to reflect the above situation. This gave rise to the use of a considerable number of extracting solutions, some of a universal character (Spryway, Morgan, etc.), others of a selective nature for the P extraction (ammonium lactate, sodium bicarbonate, ammonium fluoride, etc.).

In some cases, these extracting solutions reported a significant correlation with phosphorus plant yield, showing in this way a correct estimation of phosphorus absorption by the plant but in other cases that correlation was not obtained.

In 1.950, Wiklander (178) stated his theory concerned with labile phosphorus, by which this soil scientist explained that not all the soil inorganic phosphorus fractions intervene in the supply of phosphorus to plants but it is the labile phosphorus situated in the film which surrounds the particles of the soil, which is the immediate and unique form that passes to the soil solution, and in this way it influences the phosphorus concentration of this soil liquid phase. Some years later, E.G. Williams 1.967 (177), Fried and Shapiro 1.956, 1.957 and 1.960 (52, 53, 54) introduced the concepts related to soil factors that fovern soil fertility in relation to a nutrient; these soil factors are: intensity, quantity and capacity.

For phosphorus, the above soil factors have been defined as:

Intensity.- Phosphorus concentration in soil solution. It is equal to phosphorus extracted by water or 0.01 M calcium chloride solution.

Quantity.- It is the phosphorus existing in the solid phase that is easily transfered to the soil solution during a crop season. It is equal to the A, E and L values and, for some soil workers, to the maximum phosphorus adsorption value (Hagin et al. 1.963 (67)), maximum phosphorus desorption (Fried 1.967 (55)), % P saturation (Rennie et al. 1.957 (134)).

Capacity.- Amount of P adsorbed related to determined phosphorus concentration in final solution; that is to say, the ratio existing between the factors of quantity and intensity.

All these soil factors act simultaneously in the supply of phosphorus to a plant; however, it might be possible for any of them to become a dominant factor in this phosphorus transfer and then a crop exhibits deficiencies, due to three causes (A. Van Diest 1.969 (162)).

1) Although a soil has a high reserve of assimilable phosphorus (high quantity factor), the rate of this phosphorus solubilization is so low -- that it produces a poor renewal of P concentration in the soil solution (low intensity factor).

2) The soil has a very low reserve of assimilable phosphorus (low intensity factor), although the rate of this phosphorus solubilization is so high, however the plant requirements during the whole of the plant season are not satisfied.

3) Finally, thtat both intensity and quantity factors are low.

The use of the above mentioned extracting solutions is quite generalized; in tropical countries, the soils of which are strongly weathered (the intensity and quantity factors are therefore low) the soil workers found good correlations between plant yields and phosphorus extracted by strong solutions. In countries belonging to the temperate zone, there exists the tendency to use weak extracting solutions, there sometimes existing problems connected with the correct estimation of the phosphorus absorbed by the plant which might be due to these weak extracting solutions reflecting together in different proportions both intensity and quantity factors, such as was cited by E.G. Williams 1.967 (163).

Recently, some soil scientits (Banow N.J. 1.967 (13)); Fox L. and Kamprath E.J. 1.970 (48); Islam M.A. and A.F. Rahman 1.959 (82); Khasawruth F.E. and J.P. Copeland 1.973 (95); Ozanne P.G. and T.C. Shaw 1.968 (127); Rajan S.S.S. 1.973 (133) have mentioned that the best procedure for carrying out a correct estimation and evaluation of the phosphorus needs of a soil for an optimum crop yield, can only be through an expression that reflects these soil factors.

For Ozanne P.G. and T.C. Shaw 1.968 (124), Rajan S.S.S. 1.973 (133) and Banow N.J. 1.967 (3) that is equal to the use of an expression related to the buffering capacity of a soil, attained at a defined phosphorus concentration in final solution; while for Khasawruth F.E. and J.P. Copeland 1.973 (95) and Fox L. and E.J. Kamprath 1.970 (48) that means the use of an expression of the Langmuir isotherm that evaluates together these soil fertility factors.

CHAPTER 2

2.1. DESCRIPTION OF SARAGOSSA PROVINCE
2.2. MATERIAL USED (SOILS)
2.3. METHODOLOGY

CHAPTER 2

This chapter includes the characterization of the province of Saragossa through its geographical, climatological, geological, hydrographical, soil, ecological, and economical descriptions, in order to familiarize the reader with this province.

This chapter also contains the description of the soil material used as well as the methodology followed for laboratory determinations and experiments under greenhouse conditions.

2.1. DESCRIPTIONS OF THE PROVINCE OF SARAGOSSA

A) Geographical

The province of Saragossa is situated between the meridians 1º31' and 4º27'E of Madrid and at a latitude of 40º56' and 42º55' North; being bounded on the North by the province of Huesca and Navarra, on the West by the provinces of Soria and Navarra, on the East by the provinces of Huesca, Lerida and Tarragona and on the South by the province of Guadalajara and Teruel.

In the province of Saragossa, we can distinguish three separate natural areas. The largest is that which forms part of this same Iberian Plain, a uniformly flat region without any considerable variations of altitude (between 250 and 500 m.), relieved only by a few residual heights of erosive origin which do not, however, go beyond 700 metres in height, among which we may mention the Sierra de Alcubierre and the mountains of Castejón.

This erosive process, which is basically of fluviatic origin, is particularly intense in this region and is due to the following causes: The character of the soft, incohesive material that fills the river basin, the frequently squally character of the rainfall and, thirdly, the lack of any vegetation capable of mitigating the effects of erosion, all of which, added to the dryness of the climate, produces a semi-desert type of landscape, in which the full-flowing Ebro, as it traverses the plain, mitigates the appearance of extreme aridity which characterizes this part of the country, due also in part to the considerable concentration of gypsum in the province of Saragossa. Three large regions may be distinguished in the Iberian Plain, in which there is a predominance of gypsums. Two are to be found along the two banks of the Ebro: that which surrounds it on the North and beginning at Tauste, stretches continuously as far as Peñalba and the region to the South of the river which stretches from the neighbourhood of Borja as far as Quinto, passing through Pina and Belchite. The third gypseous area, which is a considerably narrower fringe, is confined to the province of Huesca.

In an area as vast as the Iberian Plain we naturally find, within the generally uniform character of the area, a large number of distinctive natural regions under different names; but mostly not clearly delimited. Thus we have Los Monegros (a markedly steppe-like region between the Ebro and the Sierra de Alcubierre); El Castelar (which covers the area on the left bank of the Ebro between the Rivers Gallego and Arba), the plain of Plasencia (along the right bank of the Ebro which is the area between the Rivers Huecha and Jalón); the flats of La Violada (to the North of the Ebro, along the road from Saragossa to Huesca); Las Bardenas (a dry, desert-like area situated on the borders of the provinces of Saragossa and Navarra) and, lastly, the country known as Las Cinco Villas (an eminently cereal producing area, now being completely transformed by the new irrigation work-, between the province of Navarra and the River Gallego, the Northern extension of El Castelar which stretches up to the outermost spurs of the Pyrenees).

The other two natural regions of which the province of Saragossa occupies a part are those of the Celtiberian and Iberian Sierras. One is, in fact, a prolongation of the other, with only the depression formed by the River Jalón lying crosswise between them. Together they form a series of ranges lying North-West to South-East, with an average height of 700 to 1.000 metres. Only the extreme South-Western portion of the province is included in these two natural regions, where owing to the proximity of the Ebro valley, there are gradually descending altitudes, so that the foot-hills of these two Sierra formations come to form part of the province of Saragossa. Among the ranges belonging to the Celtiberian portion, we may mention the Sierra de los Amantes and the Sierra de la Virgen, and in the Iberian portion those of Vicort, Algarión, Santa Cruz and El Salorio. The whole of this mountain system culminates in the Pico del Moncayo (2.313 metres) and belongs to the Celtiberian Sierras, on the border between the provinces of Saragossa and Soria.

Among the various natural regions which may be distinguished in this part of the province of Saragossa, we may mention, as being of special interest, the "hollow" of Calatayud, in the depression between the Celtiberian and Iberian Systems, watered by the River Jalón and the Valley of the Jiloca, by which it is watered, with Daroca as its most thriving population centre; two rich, fertile valleys producing large quantities of vegetables and, especially, fruit.

B) Climate

According to J.M. Albareda and collaborators 1.960 (1), the climate of the Ebro Valley, like any other climate, has been influenced by three groups of factors; some constant, due to the march of time, such as: the effects of solar heat; others varying in time, in relation to their formation and intensity, such as: wind and rain, and the third group; those of a geographical nature, reacting on the other two, such as: relief. Under this last heading, we may point to the inland continental character of the region, due to its relatively low-lying situation and high marginal mountain ranges enclosing the valley; a character which is expressed in its cultural and economic, as well as in its overall climatic features.

The Southern and South-Eastern region of the marginal Sierras, namely the Celtiberian and Iberian, offers a climate of fairly continental character, though with some Summer rainfall, the mean rainfall being always over 550 mm., with abundant snowfalls in the cold Winter season. But as the province of Daragossa is only affected by the foot-hills of these Sierras, the true climatic character of this zone is attenuated, so that in places where it has been taken, rainfall does not amount to 500 mm.; and the mean temperature is above the figure proper to the climatic region to which it really belongs.

The Iberian Plain: a well defined climatic region of the continental variety, with a very hard climate, very cold, dry Winters and very hot Summers, also dry. There is a primary rainfall maximum in Autumn and another, secondary masimum in Spring; however, as a general rule, the number of rainy days in the whole year does not reach 60, and the number of days on which snow falls ism at the most, two. In Autumn, the rain bearing - winds are usually North-East and South-East while during the other months of the year they are North-West and South-West. The mean temperature is - round about 14 or 15 degrees; but with very great variations of temperature, generally greater in the Northern part of the valley.

Table nº 1 summarizes the data from observations at a number of stations which J.M. Albareda and collaborators consider to be representative, grouped according to climatic regions.

Table nº 1.- Climatological data from the Saragossa Province.

Region	Station	Altitude-metres	Rainfall-mm	Temperature		
				mean annual	mean maximum	mean minimum
Iberian Plain	Epila Saragossa	336 237	310 317	15.5 15.3	21.6 20.5	7.8 10.1
Celtiberian Sierra	Veruela	650	439	13.5	19.0	8.1
Iberian Sierra	Daroca	778	421	12.6	19.0	6.3

C) Geology

According to J.M. Albareda and collaborators 1.961 (1), in the - province of Saragossa we can distinguish two geological areas, one formed by Tertiary terrains belonging to the Iberian Plain, the other consisting of older material forming the Celtiberian and Iberian chains, with the depression of the River Jalón in between.

If we consider both Sierras as forming a whole, they consist of a series of parallel ranges running N.W. to S.W. which we shall call the Iberian chain. This chain begins in the Sierra de la Demanda and it branches out, just after the point at which it enters the province of Saragossa, into two separate chains divided from one another by the Tertiary depression of Calatayud, a river-basin which follows the course of the Jiloca - and extends as far as Teruel. Of these two brances the easternmost will be called the Eastern Iberian Chain, and the other, naturally, the Western Iberian Chain.

They form a geological whole of considerable stratigraphic complexity, consisting of Mexoic terrains lying upon a Palaezoic substratum, basically of slate and quartzites, which form, on the emergence of the nucleus of a series of anticlinal folds of Saxon type parallel to the main line of the chain.

We can distinguish three important Palaezoic zones: a North-Eastern which extends from the North of Tabuenca to the North-East of Mesones, a middle zone starting from the Moncayo area and following the Sierras, - de la Virgen, de Alguiren and de Herrera into the province of Teruel, at Montalbán and thirdly, another further West and including the Western Iberian chains which, beginning at Almenar in the province of Soria, passes through Ateca and stretches as far as Calamocha in the province of Teruel.

This Palaezoic formation consists of Cambrian and Silurian and some Devonian terrains which, starting at Montalbán in the province of Teruel, extends into that of Saragossa in the neighbourhood of Luesma. In the latter province, no Archean or Pre-Cambrian terrains are found, the two insignificant patches of igneous rocks to be found between Luesma and Herrera being probably Silurian.

Within the Mesozoic, we find materials of basically Triassic origin, represented by Kemper clays and iris marls and by multi-coloured Bunt sand stein type sandstones, without any middle Trias or Muschelchalk, owing to tectonic phenomena.

On the other hand, the Triassic and Surassic are very uncvenly represented in this portion of the province of Saragossa. The cutaceous, consisting mainly of hard limestones and also marls with banks of limestone no doubt belonging to the Upper Cenomanian, Turonian and in part, Senonian is found in the form of a long strip running from North-West to South-East through Alhama and widening out towards Campillo.

Most of the Tertiary throughout this region belongs to the Upper Tertiary and covers, in the Calatayud depression, from Saunatian to Pontian showing a great variety of lithological facies, since we find here gravels, sandstones, marls, limestones and gypsums.

The rest of the province of Saragossa belongs to the Ebro valley, which, during Tertiary times, was filled up with sedimentary material; most of it covered during the Miocene, The Oligocene being confined to the West and North of the province. Apart from the Tertiary we find only a small patch of Triassic limestones to the North of Herrera and South of Belchite. All these Tertiary materials, especially the marls, sandstones and limestones have been covered over throughout wide areas with a stratum of allochthonous stony soil during Quaternary times, giving rise to low moorlands, terraces and solifluction deposits.

D) Hydrographical

The Ebro is the most important river on the Mediterranean side of the Iberian watershed. The course of the Ebro has been divided into three reaches according to the topographical and geological characteristics of the terrains through which it passes, with a further division of the middle reach into three areas; the first stretching from Conchas de Haro to Tudela, the second from Tudela to Saragossa and the third from Saragossa to Mequinenza. In this middle reach, the river flows at an altitude of - 184 metres and three terraces are observable along the left bank at 15,40 and 65 metres above the river-bed. On the left bank, at its confluence - with the River Gallego, there is a terrace high up above the river, at - 130 metres, the layers of gravel being 10 metres thick at this point.

Of the tributaries of the Ebro along the right bank flowing into it, before it reaches the city of Saragossa, the most important is the - Jalón, which is of considerable geographical significance, forming a depression cutting across the Iberian Sierras and constituting the source - of the largest volume of water reaching the Ebro on its right bank. In its uppermost reach, the Jalón flows through Triassic marles and then through sandstony limestones; but a little before it enters Saragossa it begins to flow over Miocene sediments and the valley opens up. At Alhama it cuts - through a strip of Cretaceous and then continues through a narrow gorge - carved out of Palaezoic materials and so through Ateca, where it widens out again. At Calatayud it widens out further and joins the Jiloca, this last reach passing through terrains of Tertiary formation. Between this - point and Ricla, the river valley narrows again, and eventually comes out into the Iberian Plain at La Almunia and empties its waters into the Ebro near Alagón.

The principal tributaries of the Jalón are: The Deza, Carabantes, Ribota and Isuela which flow into it from the left, and the Piedra, Masa and Jiloca flowing in from the right. The last named is the most important and covers a total distance of 265 Km. from its source in the province of Teruel to its confluence with the Jalón in the neighbourhood of Calatayud.

Another tributary of the Ebro within this same reach is the Huecha. It collects the waters flowing down the Eastern slopes of the Moncayo and flows into the Ebro near Mallén. Below the city of Saragossa, still on the right bank, four more tributaries empty into the Ebro: the Huerva (which rises in the Sierrra Pelarda near Daroca), the Aguas Vinos (which passes through Belchite), the River Martín (which flows into the Ebro near Escatrón) and the Guadalope (its source is in the Maestrazgo and it joins the Ebro at Caspe).

It is, however, the left bank tributaries that supply most of the considerable wolume of water carried by the Ebro and at the same time, regulate its flow, supplying especially at the end of Spring and during Summer, the diminished volume entering from the right bank tributaries, which are low at this time of the year. In addition, these rivers all coming down from the Pyrenees, often pass through gorges or other valleys, thus facilitating the construction of dams and reservoirs so that a plentiful supply of electric power can be obtained from them as well as the reserves of water that are needed for all the new irrigation works in Aragón. Of all the tributaries, we refer to the most important ones: the Alagón, the Arba, the Gallego and the Cinca-Segre System, though the latter river flows almost entirely through Lérida, entering Aragón, after joining the Cinca very near the point where it empties into the Ebro.

The River Aragón rises in the Coll de Portalet (Huesca). It is fed along its right bank before it enters the province of Navarra, by four tributaries: Lubierre, Estanum, Aragón Subordan and the Veral. Among the most important tributaries along the left bank we have: Gas, Rigel and Onsella.

The River Arba rises in the Sub-Pyrenean mountain slopes, its basin consisting of the region known as Cinco Villas and empties into the Ebro near Tauste.

The Gallego rises in the Pyrenean heights of Sallent and Panticosa, flows across the depression at the foot of the Pyrenees and, cutting its way through the Sierra de Loarre, comes out into the Iberian Plain and empties into the Ebro on a level with the city of Saragossa.

The Cinca rises in the "tres Sorores"; this river takes its course Southwards, receiving the waters of the Esera at Grado, flows into the Oligocene Plain and just before it reaches Fraga, receives the tributary Alcandre. Shortly after this, it joins the Segre with which it very soon flows into the Ebro near Mequinenza, making the total course of the Cinca about 150 Kms.

E) Soil Survey

The description of the soil types of the Saragossa province as well as their cartography at 1: 300.000, was made by J.M. Albareda, A. Guerra, F. Mountoriol un 1.961. In 1.970, the Alonso de Herrera and José Mª Cuadrado Trusts, belonging to the High Council of Scientific Research, have published maps and reports concerned with the provinces of Huesca and Saragossa.

A photographic reproduction of this soil map has been included, in order to supply information about the main soils of the province of Saragossa.

F) Ecology

The middle basin of the River Ebro, among the counterforts of the Pyrenees, the littoral Sierras and the Iberian System, remains isolated from the influence of the humid maritine winds and for that reason it presents a steppe-like climate.

The xerical aspect of the plants and vegetal communities expresses the particular character of the dominant climatic conditions.

The appearance of the vegetal covering and its flora composition seems like that of the Mauritanian steppes owing to the resemblance of the ecological conditions.

The climate of this area is reflected by the phytosociological groups of the "estipula" (Lygeo-Stipetalia order), and Spanish grass steppes as well as those of Sisallares (Solsolo-Peganetalia order), the hyper-halophyla vegetation (Limonietalia order) and the Tamarix (Tamaricetolia order).

The units of Botanic Taxomony (class and orders) comply with those of the Mediterranean littoral.

In this area we can distinguish three concentrical belts of vegetation arranged around the centre of aridity situated between the city of Saragossa and the Monegros Area.

These vegetation belts are:

a) The sabine grove (Rhamneto-Cocciferetum thuriferetosum).
b) Pine grove with quercus coccifera ("coscoja"). (Rhamneto-Coccìferetum coricetomus humilis, pistacietomus and cociferetomus).
c) Cork-oaks grove (Quercetum rotundifoliae).

From a to c, the dryness of the climate decreases as a consequence of increase in humidity owing to the rise in altitude or to the proximity of the littoral.

The climax of the sabine grove from low plains has been disturbed by man. The forest of Rhamneto-Cocciferetum has completely disappeared and in its place we found a steppe-like vegetation and crops. In the areas where the soil profile development is complete, the Spanish grass is present, while in the litho-soils rosemary is the natural vegetation.

Both areas are used under dry farmihg with crops such as cereals.

g) Economic

The economic development of the province of Saragossa as of the rest of Spain, depends upon a multitude of causes difficult to enumerate in this section, in which we propose only to point out the main sources - of economic wealth which form the bases of the development now taking place.

The province of Saragossa belongs to an eminetly agricultural region fo Spain called Aragón, and it is therefore this aspect which marks its economic development and it is with a view to obtaining an increase of agricultural produce that the present irrigation projects are being advanced. At the same time, however, an effort is being made to increase - the production of electric power, the basis of industrial progress, by harnessing the waters of the Pyrenean rivers to the full.

These are the two aspects, namely, an increase of agricultural - produce and a greater volume of hydro-electric reserves, on which the economic policy at present applied to Aragón is based in its general outlines.

The irrigation works of the Ebro basin constitutes one of the most ambitious hydraulic projects in Europe and they are based on the joint harnessing of the most important rivers flowing through it and of the torrential Pyrenean streams by means of a close network of reservoirs such as - those of Yesa, Val de la Fuen, San Bartolomé, La Peña, Sotonera, Mediano and Barasona. This will involve, besides, changes in the cropping pattern of the area, in which industrial crops, fruits and vegetables will be more intensively cultivated at the expense of cereals which, along with the vine and the olive, constitute the three stable froms of dry farming production in Aragón.

According to agricultural production the province of Saragossa is divided into the following areas:

1. Cinco Villas

From an historical point of view this area forms a unit; however, economically and geographically it includes two sub-areas.

1.1. Sos del Rey Católico

It is situated to the North of the province of Saragossa, with a mountainous topography and litho-soils where agriculture is based upon cereals.

1.2. Ejea de los Caballeros

Formerly, this area was dedicated to cereals under dry-farming; but nowadays irrigation projects have changed this agriculture towards vegetables and industrial crops (alfalfa, maize) because this area is irrigated by the Bardenas Canal that proceeds from the Yesa Reservoir. (This may be considered as an example of what was mentioned above about changes in the cropping pattern due to irrigation).

2. Borja-Tarazona

It is situated on the borders of the provinces of Saragossa with the province of Navarra. It is formed by smaller flats, terraces and sierras. Agriculture is concerned with: alfalfa, potatoes, olives and wheat.

3. Calatayud

Depression watered by the River Jalón, between the Iberian and Celtiberian Systems.

It is well-known for crops such as: fruit-trees (apple) and vineyards.

4. La Almunia - Cariñena

This area includes the sub-areas:

4.1. Almunia - Epila - Morata

Where the main crops are: fruit-trees (peach, pear).

4.2. Cariñena

Situated between the Rivers Huerva and Jalón, it is the wine growing area of the province of Saragossa.

5. Campo de Zaragoza - Belchite

It includes:

5.1. The so-called Campo de Zaragoza, that is to say, an area situated in the South-West of the province of Saragossa, formed by terraces of the Rivers Ebro, Jalón, Huerva and Gallego where the main crops are: vegetables and fruits.

5.2. Belchite

The worst area of the province of Saragosse for agricultural purposes because the dry weather conditions together with the altitude and the great accumulation of gypsums in its soils, allowing only for wheat and olive production.

6. Daroca

It corresponds to the valley of the River Jiloca and Campo de Romanos, both dedicated to: vineyards, fruit-threes and cereals.

7. Caspe

This is the transition area between Aragón, Catalonia and Levante. The main crops are: cereals and olive. In table nº 2 can be seen the total yields as well as the surface used (in ha.) for the above mentioned economic areas of the province of Saragossa.

Table nº 2.- Crops in the economic areas of the Saragossa province.

C r o p s		Surface used (in hectares)							Total yield (in Qm)
		Economic areas of the Saragossa Province							
		1	2	3	4	5	6	7	
Wheat	dry farming	43,839	11,742	20,643	19,878	79,835	23,754	13,538	1.177,000
	Irrigated	5,439	3,601	1,574	586	11,595	600	849	798,500
Barley	dry farming	33,249	5,828	7,195	9,972	47,472	9,400	29,230	1.335,000
	Irrigated	8,500	2,301	1,019	451	4,058	304	1,475	326,500
Maize		9,623	4,521	1,086	3,478	23,582	-	2,080	1.716,000
Alfalfa		9,287	1,045	1,204	1,533	13,176	-	837	7.912,400
Onion		719	-	-	-	926	-	-	1.108,200
Potato		491	756	-	-	-	-	-	643,300
Tomato		-	308	-	-	-	-	-	509,910
Pepper		-	584	-	-	-	-	-	177,140
Sugar-beet		4,499	-	-	-	-	-	-	1.950,500
Apple		-	-	2,479	2,878	420	-	-	865,720
Pear		-	-	976	793	900	-	-	274,340
Peach		-	-	556	475	604	-	-	80,360
Grapes		-	-	24,513	36,474	4,754	5,600	2,704	1.292,890
Olive		-	-	-	-	1,376	-	9,162	262,870
Almond		-	-	3,424	1,400	302	-	5,158	97,640

Note: The maize, alfalfa, sugar-beet, vegetables and fruit-trees are cultivated under irrigation and olive and almond under dry-farming.

2.2. SOIL MATERIAL

In chapter 1 it was pointed out that we require to have a knowledge of the phosphorus status in the soils of the province of Saragosse. For that reason, we have chosen four calcareous soils (gypsum serosem, marly serosem, terrace soil and alluvial meadow soil) due to the fact that the above soils are situated in notable areas of the province of Saragossa - and as a reference a non calcareous soil belonging to a locality in this province.

A soil sampling was carried out, in which soil profiles were situated in the most representative areas of the same; for this purpose Dr. - Francisco Alberto (head of the soil classification section at Aula Dei) advised how to do this. In 1.971, this choice was checked and confirmed by some members of the staff of the soil science department at Gembloux University.

Every soil profile was characterized by its morphological, chemical and physical descriptions. These are included.

In general, the Ap horizon is variable in short distances (Tisdale). An intensive soil sampling of this horizon was made; that is to-say, practically the whole soil volume included in the 1 square metre surface where the soil profile was situated was taken up.

This soil material was well mixed, dried and sieved through 2 mm., and again mixed. This well-mixed soil material was used for the greenhouse trials and P adsorption and desorption procedures at the Laboratory.

A) Soil description

1. Gypsum serosem

Place .... Alfajarín (Saragossa province)
Position .... Farm belonging to Mr. Escanero, in a plot - 10 metres from the house.

Altitude .... 300 metres above sea-level.

Topography .... Flat.

Drainage .... Excellent.

Erosion .... Slight accumulation of sediments.

Natural vegetation .... Helianthenum squamatum, repidum subulatum, herniaria fruticosa, gypsophula hispanica, ononis tridentata, stipa barbata, eremorpyrum cristatum, thymus vulgaris, etc.

Agriculture .... Fallow of wheat.

Geology .... Gypsum of miocene and slight accumulation - of sediments.

Morphology

Depth (cm.)	Horizons	
0- 50	Ap	Abundant roots and earth worms. müll (2.12% O.M.) Textural class: clay Gravel (5%) Sub-poliedric-poliedric structure Good permeability Porous and canalicules disturbed by earth-worms. Colour 10 YR 6/2 (dry). Degree of humidity: dry.
50- 80	$A\ h_2$	Limited roots and some earth-worms. müll (1.448% O.M.). Textural class: clay. Sub-poliedric structure with small aggregates (size 4 mm.). Very good permeability. Large pores Colour 2 Y5/4 (dry) Degree of humidity: dry.
80-115	C_1y	There are no roots. Accumulation of gypsum Textural class: clay Sub-poliedric structure with small aggregates (size 4 mm.) Degree of humidity: fresh
115	C_2	Parent material

2. Marly serosem

Place	Sierra de Luna (Saragossa province)
Position	On the hill side.
Altitude	300 metres above sea-level.
Topography	Slightly undulated.
Drainage	Slightly impeded.
Natural vegetation	Pistacia lenticus, Rhemus infectoria, Tymelaca finctorea, Berxux sempervivens.
Agriculture	Fallow of wheat.
Geology	Sediments of sandstones and marles.

Morphology

Depth (cm.)	Horizon	
0-45	Ap	Abundant roots and earth-worms müll (1.137% O.M.) Textural class: clay Sub-poliedric structure with a hard consistency Moderate permeability Abundant pores Colour 2 YR 6/2 (dry) Degree of humidity: dry
45-62	A h_2	Some roots and abundant earth-worms. Textural class: clay Sub-poliedric structure with a hard consistency Moderate-slow permeability Colour 2 Y 5/4 Degree of humidity: fresh.
62-80	C_1	Some roots. Textural class: clay Apoliedri structure Slow permeability Impeded drainage Abundant capilar pores Organic matter accumulated through cracks Colour 5 Y 6/4 Degree of humidity: fresh.
80-100	D_1	Some roots. Textural class: clay Prismatic structure with mottling inside aggregates Poor permeability. Impeded drainage Some capilar pores Colour 5 Y 6/1 and 10 YR 5/3 (mottling) Degree of humidity: fresh.
100	D_2	Hydromorphic horizon

3. Soil developed on terrace

Place	Farm belonging to the Experimental Station of Aula Dei, Saragossa province (San Bruno).
Position	100 metres from the border of the lowest terrace.
Altitude	300 metres above sea-level.
Topography	Level ground
Drainage	Excellent
Natural vegetation	Inula viscosa, Sanquizorla magnolie, Ononis natrix, Chenopodium boytrus, Andryla ragusina.
Agriculture	Sugar-beet - maize and wheat.
Geology	Sandstones.

Morpholoy

Depth (cm.)	Horizon	
0-42	Ap	Abundant roots mÜll (1.413% O.M.) Textural class: clay loam Poliedric-sub-poliedric structure Excellent permeability Intermediate and small pores Colour 10 YR 7/3 (dry) Degree of humidity: dry.
42-55	Bv	Abundant roots Textural class: sandy-clay-loam 35% of stones (of which 20% is gravel) Sub-poliedric structure Excessive permeability Colour 10 YR 5/4 Degree of humidity: wet
55	Ca	Some roots Textural class: sandy with 75% stones (of which 25% is gravel) Crushing structure Colour 10 YR 5/4 Degree of humidity: wet.

4. Alluvial meadow soil from the River Gállego

Place	Plot in the Campus of the Experimental Station of Aula Dei (Saragossa province).
Position	Middle of terrace at 20 m. from the border of highest terrace.
Altitude	300 metres above sea-level and 7-9 m. above the bed of the River Gallego.
Topography	Flat.
Natubal vegetation	Inula viscosa, Sanguisola magnolie and soon.
Geology	Sediments brought by the River Gallego

Morphology

Depth (cm.)	horizon	
0- 40	Ap	Presence of roots MUll (1.499% O.M.) Textural class: clay Poliedric structure Good permeability Abundant pores, canalicules and fissures Colour 10 Y 7/2.5 (dry) Degree of humidity: dry
40-100	B	Presence of roots Textural class: clay Sub-poliedric structure Moderate permeability Drainage slightly impeded Intermediate pores and canalicules Colour 10 YR 5/4 (wet) Degree of humidity: wet
100-120	M_1	There are no roots Textural class: clay Poliedric structure Moderate permeability. Drainage slightly impeded Presence of a diffuse mottling that shows an irregular shape Colour 10 YR 5/4 and 10 YR 5/6 (mottling) Degree of humidity: fresh

+ 120	M_2	There are no roots Textural class: clay Poliedric structure with a hard consistency Moderate permeability Colour 10 YR 5/4 Degree of humidity: fresh

5. Brown soil

Place	At 250 metres N. of Agramonte Sanatorium (Moncayo Saragossa province).
Position	Top of declivity.
Topography	Concave and convex (declivity of a mountain).
Altitude	600 metres above sea-level.
Microrelief	Slightly undulated.
Vegetation	Coniferous
Geology	Parent material formed by sandstones and slates. These materials are mixed in situ with some gravels carried by morraines.

Morphology

Depth (Cm.)	Horizon	
0- 45	Ap	Abundant roots müll (1.396% O.M.) Textural class: sandy loam Stoniness 5-10% (of which 20% is gravel) Slightly plastic Sub-poliedric structure Good permeability Abundant fine pores Colour 7.5 YR 6/4 (dry) Degree of humidity: dry
45- 90	Bv	Some roots Textural class: Sandy loams Stoniness 5% (of which 10-15% is gravel) Plastic and sticky Sub-poliedric structure Good permeability Colour 5 YR 4/5 (wet) Degree of humidity: wet

90-100	Bc Cv	Some roots Textural class: Loam Stoniness 40% Slightly plastic and sticky Sub-poliedric structure Good permeability Abundant pores (intermediate size) Colour 5 YR 4/6 Degree of humidity: fresh
110	Cv	Parent material, slightly weathered.

B) Chemical features

All these soil horizons were analysed at the laboratory according to several procedures in order to know their chemical and physical features. In all these laboratory procedures two replicates were used.

For the chemical features of these soils the following laboratory determinations were used:

1. Reading of pH

In water and 1N potassium chloride solution with a ratio soil: solution (1:2), after a shaking time of 20 minutes, the soil was read on a Beckman DV pH meter. The pH values are:

Table nº 3.- pH values

Soils	Horizons			
Gypsum serosem	Ap	A h_2	C_{1y}	C_2
	7.95	8.00	8.00	7.60
	7.60	7.65	7.95	7.70
Marly serosem	Ap	A h_2	Bp	D1
	8.32	8.40	8.40	8.50
	7.90	7.95	7.90	8.10
Soil developedon terrace	Ap	Bv	Ca	
	7.35	7.40	7.35	
	7.75	7.95	8.00	
Alluvial meadow soil from River Gállego	Ap	B	M1	M_2
	7.30	7.40	7.35	7.30
	7.70	7.65	7.65	7.65
Brown soil	Ap	Bv	Bv cv	
	7.50	8.05	7.80	
	7.65	7.90	7.70	

The former data is pH in water and the other is in potassium chloride solution.

All the soils are neutral or slightly alkaline, this pH data increasing along the soil profile in the majority of these soils (please see the pH figures obtained in 1N potassium chloride solution).

2. Total calcium carbonate and free calcium carbonate determinations

For these determinations, the Barnard and Dromineau G. 1.951 (45) procedures were used.

In Table nº 4 these contents expressed in % can be seen.

Table nº 4.- Total calcium carbonate and free calcium carbonate contents (in %)

Soils	Horizons			
	Ap	A h_2	C_1y	C_2
Gypsum serosem	24.09	26.29	44.10	13.68
	12.50	14.90	16.10	7.20
	Ap	A h_2	Bp	D_1
Marly serosem	36.54	33.85	42.84	55.86
	12.06	13.68	15.50	14.37
	Ap	Bv	Ca	
Soil developed on terrace	23.43	22.26	31.50	
	12.40	9.12	12.20	
	Ap	B	M_1	M_2
Alluvial meadow soil from River Gallego	30.77	25.36	26.04	28.72
	13.80	14.70	13.50	13.40
Brown soil	It does not contain			

Of the five soils studied, only the brown soil does not contain calcium carbonate, the rest of these soils show calcium carbonate - values, for which there is no doubt concerning their calcareous nature.

In soils (Terrace and marly serosem) this calcium carbonate content increases along the soil profile; the alluvial meadow soil of the - River Gállego has similar calcium carbonate values in the deepest soil - horizon and in the gypsum serosem the C_2 horizon shows the lowest value of total calcium carbonate.

The free calcium carbonate data in all soil horizons is similar.

3.Organic carbon determination

The Wakley and Black method 1.934 (167) is followed and the organic matter value is obtained using the factor 1.724. This data can be seen in Table nº 5.

Table nº 5.- O.C. and O.M. values respectively expressed in %.

Soils	Horizons			
Gypsum serosem	Ap	A h_2	C_{1y}	C_2
	1.23	0.84	0.34	0.09
	2.12	1.448	0.586	0.155
Marly serosem	Ap	A h_2	Bp	D_1
	0.65	0.44	0.27	0.20
	1.137	0.761	0.482	0.362
Terrace soil	Ap	Bv	Ca	
	0.82	0.51	0.39	
	1.413	0.896	0.672	
Alluvial meadow soil from River Gallego	Ap	B	M_1	M_2
	0.87	0.38	0.30	0.31
	1.499	0.672	0.517	0.534
Brown soil	Ap	Bv	Bv cv	
	0.81	0.39	0.52	
	1.396	0.672	0.896	

In all calcareous soils, the O. Carbon and O.M. contents derease along the soil profile while in the brown soil the Bv cv horizons has an intermediate content between those obtained for the upper horizons (Ap and Bv).

4. Total nitrogen

The Kjedahl method (130 a) was used, using selenium as a catalizer and after that a macrodistillation followed with the respective valuation. This total nitrogen data was expressed in % and can be seen in table nº 6.

Table nº 6.- Total nitrogen conten (in %)

Soils	Horizons			
	Ap	A h2	$C_{1}y$	C2
Gypsum serosem	0.151	0.042	0.056	0.014
	Ap	A h2	Bp	D_1
Marly serosem	0.056	0.064	0.047	0.039
	Ap	Bv	Ca	
Soil developed on terrace	0.123	0.095	0.056	
	Ap	B	M_1	M_2
Alluvial meadow soil	0.131	0.126	0.075	0.067
	Ap	Bv	Bv cv	
Brown soil	0.08	0.064	0.084	

In all soils studied, the distribution of total nitrogen was similar to that of organic matter in these soils.

In order to know what the situation is of this total nitrogen in these soil horizons, the ratio C/N was used. These C/N values were included in table nº 7.

Table nº 7.- C/N data in soil horizons

Soils	Horizons			
Gypsum serosem	Ap	A h_2	C_1y	C_2
	8.10	20	6.0	6.4
Marly serosem	Ap	A h_2	Bp	D_1
	11.40	6.9	6.0	5.0
Soil developed on terrace	Ap	Bv	Ca	
	6.3	5.3	7.7	
Alluvial meadow soil from River Gallego	Ap	B	M_1	M_2
	6.6	3.0	4.0	4.6
Brown soil	Ap	Bv	Bv cv	
	10.1	6.0	6.1	

This C/N data, in all soil horizons (except A h_2 in grypsum serosem) was lower than 10, meaning that there exists a process of active mineralization for the organic matter of these soils.

5.Soluble salts

A ratio soil: water (1:5) was used, the electric conductivity of this extract was read and this lecture was corrected by the factor of temperature, this data being expressed in mmhos/cm.

The above figures mean the non-existence of salinity problems in these soils.

Table nº 8.- Soluble salt data

Soils	Horizons			
	Ap	A h_2	C_1y	C_2
Gypsun serosem	0.585	0.475	0.625	0.550
	Ap	A h_2	Bp	D_1
Marly serosem	0.937	0.862	1.00	1.23
	Ap	Bv	Ca	
Soil developed on terrace	0.705	0.63	0.597	
	Ap	B	M1	M2
Alluvial meadow soil from River Gallego	1.29	0.789	0.795	0.725
	Ap	Bv	Bvcv	
Brown soil	0.637	0.962	0.975	

6. Assimilable potassium

This element was extracted by 1N ammonium acetate solution, buffered at pH 7.0, in a ratio soil: solution (1:10) and shaking time of 15 minutes. The soil suspension was filtered through Whatman paper and the potassium content was analysed by photometry.

These potassium values were expressed in mg. K_2O/100 g. of soil.

In the four calcareous soils, these potassium values showing that these soils are well supplied in this nutrient, while the brown soil had a low content.

Table nº 9.- Assimilable potassium content expressed in mg. K20/100 g. soil

Soils	Horizons			
Gypsum serosem	Ap	A h_2	C_1y	C_2
	47.50	30.00	11.50	6.50
Marly serosem	Ap	A h_2	Bp	D_1
	135.00	90.00	28.00	18.00
Soil developed on terrace	Ap	Bv	Ca	
	38.00	22.00	12.00	
Alluvial meadow soil	Ap	B	M_1	M_2
	48.50	37.00	26.00	30.00
Brown soil	Ap	Bv	Bvcv	
	3.50	2.50	2.50	

C) Physical features

At the laboratory the following determinations were made:

1. Mechanical analysis

According to the method of Robinson's pipette, using peroxide for the organic matter destruction and sodium hexametaphosphate as a disperser.

The distribution of soil particles according to their size and expressed in % can be seen in Table nº 10.

Table nº 10.- Mechanical analysis

Particle size distribution									
Soils	Horizons	2000 630μ	630- 200μ	200- 63 μ	63- 20 μ	20- 6.3μ	6.3- 2 μ	> 2μ	Textural class
Gypsum serosem	Ap	0.09	0.50	1.53	6.30	11.81	26.09	53.68	Clay
	A h_2	0.61	0.74	2.28	13.08	15.11	18.8	50.00	Clay
	C_{1y}	1.76	1.28	3.71	17.06	11.80	14.19	50.20	Clay
Marly serosem	Ap	0.23	4.63	18.39	14.13	10.89	11.73	40.00	Clay
	A h_2	0.48	0.58	19.33	11.00	9.83	15.83	43.96	Clay
	B	0.45	0.55	19.33	10.00	10.83	15.92	43.82	Clay
	D1	0.40	0.60	19.00	10.00	12.00	16.00	42.00	Clay
Soil developed on terrace	Ap	0.18	2.23	6.59	18.91	15.10	20.78	36.21	Clay loam
	Bv	2.81	8.46	12.58	25.42	9.18	12.63	26.92	Sandy clay loam
Alluvial meadow soil from River Gállego	Ap	0.38	1.44	7.16	16.88	15.93	17.30	40.91	Clay
	B	0.16	0.02	0.71	7.60	8.93	22.43	60.15	Clay
	M_1	0.23	0.60	2.45	11.31	13.12	15.25	57.04	Clay
	M_2	0.24	0.61	4.68	14.67	13.05	17.04	49.71	Clay
Brown soil	Ap	2.92	6.24	27.39	28.30	13.49	7.73	13.93	Sandy loam
	Bv	2.81	5.90	24.73	26.80	14.86	10.50	14.40	Sandy loam
	Bvcv	0.88	3.41	19.30	20.40	19.53	15.14	21.34	Loam

Gypsum serosem, marly serosem and alluvial meadow soil have in all their soil-horizons a clay texture; while the soil terrace has a clay loam texture in Ap horizon but in the deepest horizons coarser textural -fractions dominate. The brown soil shows the tendency inverse to that of the terrace soil.

2. Bulk density

Non disturbed soil samples were taken up by cylinders of known volume. These soil samples were introduced into a muffle at 105º C and afterwards they were weighed.

According to the formula:

$$\text{Bulk density} = \frac{\text{Weight}}{\text{Volume}}$$

These bulk density values can be seen in table nº 11.

Table nº 11.- Bulk density values

Soils	Horizons		
Gypsum serosem	Ap	A h_2	C_1y
	1.336	1.336	1.466
Marly serosem	Ap	A h_2	B
	1.710	1.710	1.769
Alluvial meadow soil	Ap	B	M_2
	1.660	1.660	1.720

In these soils, these bulk density figures comply with the features observed in the field, which were described in the morphology of these soils.

In the terrace soil and brown soil, only the bulk density can be calculated in their Ap horizons because in the other horizons it was not possible to take undisturbed samples -owing to the presence of coarser elements.

3. Field holding capacity

By means of a Richard's apparatus and its technique. These values of field holding capacity were expressed in % on the basis of weight and they were included in table nº 12.

Table nº 12.- Data of Field Holding Capacity

Soils	Horizons		
Gypsum serosem	Ap	A h_2	C_1y
	10.03	10.03	19.90
Marly serosem	Ap	A h_2	B
	15.89	15.89	15.33
Alluvial meadow soil	Ap	B	M_2
	20.89	20.89	17.35

In the Ap horizon of the brown soil and terrace soil, these field holding capacity were 18 and 20 % respectively.

2.3. METHODOLOGY

This part includes all the laboratory procedures followed for the analysis of phosphorus as well as the technique used in the greenhouse trials.

A) Total phosphorus

The total phosphorus of the soil can be extracted by two methods, one is fusion with calcium carbonate and the other is through percloric digestion. This latter method was chosen because it is well-known for its easy handling and reproductibility.

This laboratory has been described by M.L. Jackson 1.957 (87) as follows: " 2 g of soil sieved through 1 mm. is placed in a 500 cc Kjedahl and 30 cc peroloric acid at 60% is added. During 1 hour the soil sample is digested at a temperature of 130ºC. After this tome the digestion of the soil sample is complete since the soil sample is completely white. The Kjedahl was left cooling and 50 cc water is added and this soil suspension is filtered (Whatman paper nº 42) through a funnel placed on a 200 cc volume flask. This Kjdahl was washed several times with small portions of water, each time this disolution being transferred to the 200 cc volume flask. Finally, this volumentric flask is made up to 200 cc and its contents were well mixed. An aliquot (10-20 cc) from this filtrate was taken up for the phosphorus analysis.

Colourmetric procedure

This aliquot was analysed according to the ammonium vanadate-molybdate method (M.L. Jackson 1.957 (87)). This colourmetric method consists of:

Reagents

1. Ammonium molybdate solution.- 25 g. of ammonium molybdate were dissolved in 400 cc of hot water.
2. Ammonium vanadate solution.- 1.25 g. of ammonium metavanadate were dissolved in 300 cc of water and 250 cc ClH was added. This solution was well mixed.
3. Mixed reagent.- The above ammonium molybdate solution was transferred into a 1 litre volumetric flask and after that the ammonium vanadate solution was added. Both solutions were well mixed and it was made up to 1 litre with water, keeping this solution in a dark flask.
4. Phosphate solution.- 0.383 g. of $K H_2 PO_4$ were dissolved in 1 litre of water. This solution has 200 mg. P_2O_5/litre.
5. Diluted phosphorus solution.- From the above solution, 50 cc was taken up and diluted to 100 cc with water. This solution has 100 mg P_2O_5/litre.

Colour developing

A 10 cc aliquot of filtrate is introduced into a 50 cc volumetric flask and 20 cc of mixed reagent is added. The volume is made up to 50 cc with water. After 30 minutes, the colour is read at 420 nm (Beckman DV).

For the series of phosphorus standards, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 cc of the diluted P solution were taken up and the same operation is carried out as above mentioned for the filtrate.

B) Organic phosphorus

The methods used for the soil total organic phosphorus determination are indirect and they are based on the difference between total phosphorus and total inorganic phosphorus. These methods consist of:

1. Extraction procedures

a) In these, organic phosphorus is equal to the difference between total phosphorus content and that of inorganic phosphorus, obtained generally by acidic and alkaline treatments (Menta et al. 1.954 (111)).

b) As the difference between the total phosphorus extracted by percloric digestion and the inorganic phosphorus obtained by 6N sulphuric acid (Hanotiaux (76)).

2. Ignition methods

1 g. of soil was incinerated at 500º C in a muffle during 2 hours and another equal quantity of soil were extracted by 100 cc of 2 N sulphuric acid during 1 hour. The difference of values of both extractions, according to Saunders and Williams 1.955 (139) and Hoyos and García 1.964 (82) corresponded to the total organic phosphorus.

For the estimation of this phosphorus in these five soils, the methods of Saunders-Williams and Hanotiaux were chosen because the former - is a standard method widely used by the soil workers and the latter was recommended by the professor supervising this study. The description of - both methods is included below.

Hanotiaux's method

I. Extraction and assessment of total phosphorus

Reagents

1. Percloric solution (375 cc of percloric acid diluted at 500 cc)
2. Nitric acid diluted (1:2)
3. 0.25% ammonium vanadate solution
4. 5% ammonium molybdate solution
5. Mixed reagent.- The solutions 2, 3 and 4 were mixed in equal volumes - and it followed the order of 4,3 and 2. This mixed reagent is kept in a dark flask.
6. Phosphorus solution.- 1.0984 g. of KH_2PO_4 were dissolved in 1 litre of water. This solution has a 250 p.p.mp P concentration.
7. Phosphorus diluted solution.- 50 cc of the above solution was taken up and diluted to 1 litre. From this solution equivalent amounts to (1, 2, 3, 4, 5, p.p.m. P) were taken up.

Total phosphorus extraction

2 g. of soil sieved through 0.5 mm. was placed in a 150 cc erlemeyer. This erlenmeyer was placed on a hot plate and 20 cc perclonic solution - (reagent 1) was added. The temperature of the plate was increased little by little in order to avoid explosions and quick boiling. Once the digestion of soil material was reached, the erlenmeyer was left cooling and after that, a certain amount of water was added. This dissolution was trans

ferred to a 100 cc volumetric flask. The erlenmeyer was washed several times with small portions of water which were transferred to the 100 cc volumetric flask. Until this volumetric flask was made up with water and was well mixed. An aliquot of 10 cc was taken up for the phosphorus analysis.

Colour development

This aliquot of 10 cc was introduced into a 100 cc volumetric flask and 30 cc of mixed reagent (reagent 5) was added. It was made up 100 cc - with water and well mixed.

After 30 minutes, the colour was read at 410 nm. The same was made - for the phosphorus standards.

II. Inorganic phosphorus extracted by 6 N Sulphuric acid

Reagent

1. 6N sulphuric acid solution
2. 1 N sulphuric acid solution
3. 2.5 % ammonium molybdate solution
4. Stannous chloride solution.- 2.5% (25 g. of $SnCl_2 - 2H_2O$ dissolved - in 100 cc HC_1 and diluted to 1 litre).

Extraction

1 g. of soil sieved through 100 meshes is introduced into a 50 cc Kjedahl and 40 cc 6 N sulphuric acid is added. This Kjedahl is brought up to boiling during 10 minutes. After this time, this Kjedahl is left cooling and a certain amount of water is added. After this, this solution is transferred to a 200 cc volumetric flask. The Kjedahl is washed with small portions of water twice, these solutions being again transferred to the 200 cc volumetric flask. Mix well and take up an aliquot of 10 cc for the phosphorus determination.

Phosphorus assessment

This aliquot of 10 cc was introduced into a 50 cc volumetric flask and 10 cc water was added. The pH of this extract was buffered at 3.0 - through the addition of some drops of a sodium hydroxide solution and - reading on the pH meter. After that, this solution was transferred to a 100 cc volumetric flask and 4 cc of sulphomolybdyc solution was added. - This volumetric flask was placed into a water-bath at t = 25ºC, where 3 drops of stannous chloride solution was added and immediately the colour was read at 660 nm.

The total organic phosphorus is the difference between the total - phosphorus content and that of inorganic extracted by 6 N sulphuric acid.

Saunders-Williams procedure

Reagents

2 N sulphuric acid

Extraction

2 g. of soil sieved through 2 mm. was introduced into a crucible and it was placed in an oven at 550ºC during 1 hour. After this time the crucible was removed and left cooling, its contents were transferred to an erlenmeyer. 100 cc of 2 N sulphuric solution was added. Another 2 g. soil sample sieved through 1 mm. was introduced into another erlenmeyer and 100 cc of sulphuric acid solution was added.

Both erlenmeyers were shaken during 1 hour. And after that these - soil suspensions were filtered through Whatman paper 42.

An aliquot of 2 or 5 ml was taken up for the phosphorus analysis. The phosphorus determination in both extracts was carried out through the Burriel Hernando method 1.947 (30).

This laboratory procedure consists of:

Reagents

1. Phosphorus solution.- 0.3834 g. of K H_2PO_4 were dissolved in 1 litre and this solution has 200 mg P_2O_5/litre.
2. Diluted phosphorus solution.- 50 cc of the above solution was taken up and diluted to 1 libre with 2N H_2SO_4. - This solution contains 10 mg. P_2O_5/litres.

3. Sulpho-molubdic solution.- 10 g. of sodium molybdate were dissolved at 1 litre with a solution 10% of sulphuric - acid.
4. Stannous chloride solution.- 10 g. og $Cl_2Sn.2H_2O$ were dissolved in 25 cc of Cl h. and it was kept in a dark - flask.
5. Diluted stannous chloride solution.- 0.3 cc of above solution is diluted to 200 cc. This solution must be prepared before being used.
6. pH indicator solution.- 0.1 g. of 2-6 dinitrophenol is dissolved in 25 cc etilic acohol and 75 cc water.
7. Diluted potassium cyanid solution.- 0.10 g. of KCN was dissolved in 1 litre.
8. 2% sulphuric acid solution

Colour development

An aliquot of (2 or 5 ml) is introduced into a 50 cc volumetric flask and 15 cc water, 2-3 drops of indicator solution and 2-3 ml. of 1N sodium hydroxide solution were added. Later, 1 or 2 drops of 2% sulphuric acid - solution were added until the above yellow colour disappeared. After that 2 cc of CN solution was added in order to avoid iron influence; the solution is mixed, and 2 cc of sulphomolybdic solution and 2 cc of diluted - stannous chloride were respectively added. It was well mixed and made up to 50 cc with water.

After 30 minutes, the colour was read at 660 nm in Beckman DV.

For the phosphorus standards 0, 1, 2, 3, 4 and 5 cc of diluted phosphorus solution were taken up and the colour development was made in the same way as described above.

C) Inorganic phosphorus in soil

In order to get information related to these inorganic phosphorus of soil forms, the soil-workers have followed methods based on the solubility criterion.These procedures can be:

1. Individual equilibrium of soils ans phosphorus minerals which are well known with solutions at different pH. After this equilibrium is reached, they have plotted a diagram of the phosphorus concentration according to pH. In this way, they can compare the shape of the soil curves with those obtained from the phosphorus minerals.

2. According to a method of gradient elutriation, the inorganic phosphorus fractions were separated. Soil samples underwent a progressive leaching with a solution that increases in acidity (from 0 to 10 N of sulphuric acid) and after that these soil curves are compared with those obtained for the phosphorus minerals. (Avnimelech and J. Hagin 1.965 (7-8)).

3. By consecutive extractions on the same soil sample with solutions such as: 1 N ammonium chloride, 0.5 N ammonium fluoride, 0.1 N sodium hydroxide, 0.5 N sulphuric acid, 0.3 N sodium citrate + sodium dithionite and 0.5 N ammonium fluoride. It is assumed that these extracting solutions remove the water soluble phosphorus, phosphates of aluminium, iron calcium and phosphorus coated by iron and occluded phosphorus aluminium respectively.

Normally, the term occluded is used to refer to the theory that the last two phosphorus are inside the iron oxides and cannot be dissolved by the first extractions (Jackson, M. 1.957 (34)). The combination of sodium dithionite and sodium citrate was used to remove the iron oxides in soils, otherwise they would have presented an excessive acidity that would be necessary in the absence of a reducent agent (sodium dithionite).

4. Aslyng 1.964 (6), Larsen and Court 1.961 (100) as well as Cole C.V. - and Olsen S.R. 1.959 (38), have used the solubility products calculated for solutions in equilibrium with soil samples and compared with the constants of solubility of known phosphate compounds.

In a system that consists of a liquid phase (solution) in equilibrium with a solid phase, the chemical potential of all the compounds is the same, therefore the potential of a solid phase will be easily calculated from the measures of the activities read in the solution (Larsen 1.967 (102)).

Thus diagrams for the known phosphorus compounds have been produced according to the drawing of the phosphate potential values (1/2 p Ca + p H_2PO_4) againts the lime potential (pH - 1/2 p Ca).

Under suitable cönditions of temperature and equilibrium time, the phosphate and lime potentials for soils have been obtained. These values were included in the above mentioned diagrams and in this way it has been possible to know the main phosphorus compounds in the soil.

In our study the following procedures were chosen:

1) The Chang-Jackson method, in order to have general information related to the soil phosphorus fractions. This procedure was chosen because it has been widely used by soil workers (Bates and Baker 1.960 (14); Kaila 1.963 (90); Hawkins and Kinze 1.965 (79), Khanna P.K. and B. Ulbrich 1.967 (94)), althrough this method has undergone the appropriate criticisms by Fife 1.957 (51) and Hanotiaux 1.964 (74) in relation to the phosphorus soluble in ammonium fluoride, as well as modifications in order to transform it into a routine laboratory procedure (Petersen and Corey - 1.967 (128)).

Other scientists have proposed a change in the use of the different extracting solutions (Williams 1.967 (175)), while Ginzberg et al. 1.971 (60) have introduced an ammonium molybdate solution to start the fractionalization sequence in order to dissolve the most soluble calcium and magnesium phosphates in the soil.

Thus, we have chosen the original Chang and Jackson method 1.957 (34) and the modification introduced in this procedure by Hanotiaux 1.964 (74) related to the pH of the ammonium fluoride solution for the extraction of P - Al.

The phosphorus analysis in the fractions soluble in ammonium chloride, sodium hydroxide and sulphuric acid was in accordance with the Burriel Hernando method 1.947 (30). The suitable pH adjustment was in order to achieve a normal colour development.

In the original Chang and Jackson procedure, the phosphorus determination of the soluble fraction in reductant is a heavy and tedious analysis, for that reason this determination was made according to the laboratory method proposed by Petersen and Corey 1.966 (128). This procedure consists of:

Reagents

1. 0.25 M Potassium permanganate.- 19.75 g. of K MnO_4 were dissolved in 400 cc water through heating in a boiling bath during 2 hours and a continuously stirring of this solution.
2. Ammonium molybdate solution in sulphuric acid.- 60 g. of ammonium molybdate were dissolved in 800 cc of slightly hot water. This dissolution was left cooling and 84 cc sulphuric acid were added. Finally, this solution was made up to 1 litre and was kept in a dark flask.
3. Stannous chloride solution in H2SO4 - HCl medium.- 0.3 g. of Cl_2 Sn. $2H_2O$ was placed in a 100 cc volumetric flask and 20 cc water was added. This solution was -

well mixed, and 5.6 cc of HCl was added to provoke the complete dissolution. And after that, 13 cc of H_2SO_4 was added and again it was well mixed and finally it was made up 100 cc. This solution must be prepared before use.

4. Sulphuric-clorhidric solution.- In a 200 cc volumetric flask, 40 cc - water, 11.2 cc were placed and well mixed; later it was made up to 80 cc with water, again mixed and 26 cc H_2SO_4 was added and mixed and finnaly the volume was made up to 200 cc.
5. Isobutilic alcohol
6. Ethylic alcohol

Colour development

In a separation funnel, 5 cc of the phosphorus soluble in 0.3 M sodium citrate was introduced and 2.5 cc of the solution 1 was carefully added. It was well mixed and left during 5 minutes. After this time, 5 cc of solution nº 2 was added and well mixed. 10 cc of isobulitic alcohol - was placed and well mixed through hand shaking during 5-10 minutes. After that, the funnel was left and the water phase was removed. On the alcohol phase 5 cc of solution nº 4 was added and well mixed during 5 minutes; at the end of this time the water phase was again removed. 5 cc of stannous chloride solution (solution 3) was introduced and again all was well mixed and the funnel was left, and the water phase was removed.

Finally, the alcohol phase was collected in a 10 cc flask, washing the funnel with ethylic alcohol and the colour is read at 660 nm.

For the phosphorus standards (20,40, 60 and 80 mg P_2O_5) the above sequence is followed.

The phosphorus soluble in 0.5 N ammonium fluoride; this determination was carried out in accordance with the Isobutilic method and a suitable addition of a 0.8 M boric acid solution to avoid the fluor interference in normal colour developing. This method was as follows:

Reagents

1. Ammonium molybdate solution.- 15 g. of ammonium molybdate were dissolved in 350 cc water and 350 cc of 10 N ClH solution were added. It was made up to 1 litre and was kept in a dark flask.

2. Stannous chloride solution.- 10 g. of Cl_2 Sn. $2H_2O$ were dissolved in 25 cc HCl and was kept in a dark flask.

3. Stannous chloride diluted solution.- 1 cc of the above solution was - diluted to 200 cc with a 1 N of HCl solution. This dissolution must be prepared before using.

4. Phosphorus solution.- 0.383 g of K H_2PO_4 were dissolved in 1 litre.

5. Diluted phosphorus solution.- 50 cc was taken up from the above solution and was diluted to 1 litre with 0.5 N ammonium fluoride solution. This solution has 10 mg P_2O_5 per litre.

6. 0.8 M boric acid solution

7. Isobulitic alcohol

8. Ethylic alcohol

9. 1 N of HCl solution

Phosphorus determination

In a separation funnel, 10 cc of soil extract was introduced and 15 cc of 0.8 M boric acid solution was added, it was well mixed and left during 5 minutes. After that, 5 cc of an ammonium molybdate solution and 10 cc isobutilic alcohol were added, all were shaken by hand during 5 minutes, and the funnel was left; then the water phase was removed and 10 cc of stannous chloride diluted solution were introduced, again the whole system was well mixed and the water phase removed. 10 cc of 1N HCl solution was introduced for washing the alcohol phase; after mixing again the water phase was removed.

Finally, the alcohol phase was collected into a 10 cc flask and the funnel was washed with ethylic alcohol, and transferred to the 10 cc flask. After that, colour was read at 660nm.

For the phosphorus standard series, 0, 1, 2, 3, 4 and 5 cc of the P diluted solutionwere taken up and made up to 10 cc with 0.5 N ammonium fluoride solution; afterwards one continues as one did before.

The phosphorus analysis for the soil extracts obtained according to the modification proposed by Hanotiaux, were those recommended by this author.

For the fractionalizating procedure of Chang and Jackson, we have general information concerning these inorganic phosphorus fractions, however if we require a deep knowledge related to the nature of these phosphorus compounds, another laboratory method must be followed. For that purpose, the procedure used by Aslyng 1.964 (6) was chosen. This method consists of: 5 g. of soil sieved through 1 mm was introduced in an erlenmeyer and 100 cc of 0.01 M calcium chloride solution was added. This erlenmeyer was placed in a shaker in a thermostatic chamber at 20ºC + 0.S., and the stoppered erlenmeyer was shaken during 24 hours. After this time, the soil suspension was filtered through Whatman 42 paper and this extract, pH and phosphorus were determined. pH through a reading in a pH meter Beckman DV and phosphorus analysed by the Burriel-Hernando method 1.947 (30).

D) Physicochemical soil properties related to phosphorus

1. Phosphorus adsorption

The laboratory procedures used have consisted of: to equilibrate increased phosphorus solutions as potassium diphosphate buffered at pH

7,0 or calcium diphosphate in a 0.01 M calcium chloride medium, et different soil ratios: solutions and equilibrium time. Thus, the phosphorus retained by soil has been considered as the difference between the P concentration added and that found in the final solution. This difference was expressed in p.p.m. or mg P per 100 g. of soil.

In order to show the phosphorus adsorption process by soil, the soil workers have used two types of adsorption isotherms. These isotherms are:

Freundlich: which has the form of:

$$X = a\ c^{b}$$

or in linear expression

$$\log X = \log a + b \cdot \log c$$

where:

X = is the amount of phosphorus adsorbed per unit of soil weight.

c = phosphorus concentration in final solution.

a and b are constants that vary among soils.

According to Larsen 1.967 (102), this Freundlich isotherm is empirical because its constants have no physical meaning owing to the fact that the phosphorus adsorption values did not follow this isotherm, when the P concentration in final solution was below 1 p.p.m. P (values given by Kontz et all 1.946).

Langmuir's isotherm

This isotherm has constants that when applied to gas adsorption on solids has a quantitative meaning.

It has the following equation: $V = \frac{Vm \quad bP}{(1 + bP)}$

or in linear form

$$\frac{P}{V} = \frac{1}{b \quad Vm} + \frac{P}{Vm}$$

where:

P = pressure
V = amount of gas adsorbed per unit of solid weight
Vm = maximum amount of gas which can be adsorbed as a monolayer.
b = a constant concerned with the energy of bonding.

The principles postulated by the Langmuir's isotherm are:

1) The energy of adsorption is constant (which implies uniform sites and no interaction between adsorbed molecules).

2) The adsorption takes place in determined sites (which implies no translational motion of adsorbed molecules in the surface plane).

3) The maximum adsorption possible corresponds to a complete monomolecular layer.

In chapter 1, it was mentioned that Olsen and Watanabe 1.957 (122) established that under 20 p.p.m. P in final solution, the phosphorus adsorption values followed the Langmuir isotherm, for that reason it is possible to calculate the maximum phosphorus adsorption as well as the energy constant related to the bonding of the phosphorus to soil particles, by using the next equation:

$$\frac{c}{X/m} = \frac{1}{K_1K_2} + \frac{C}{K_2}$$

where:

C = phosphorus concentration in final solution
X/m = amount of P adsorbed by unit of soil weight
K_1 = constant concerned with the energy of bonding between P and soil.
K_2 = maximum phosphorus adsorption.

In the same chapter 1, it was pointed out that it is the first - time that a study concerned with phosphorus adsorption is carried out and, in general, the literature cites two laboratory procedures; one consists of potassium diphosphate solutions buffered at pH 7.0 (Rennie et al. 1.959 (134)), Olsen and Watanabe 1.957 (122)), (Hagin et al. 1.963 (71)) and the latter, a medium of 0.01 M. calcium chloride with increased - amounts of calcium diphosphate (Ozanne P.G. and Shaw 1.968 (127)), (Rajan S.S. 1.973 (133)).

We have believed that the estimation of this phosphorus adsorption by both laboratory methods would be useful. For that, in the former method was used a range of phosphorus (0--40 p.p.m. P) in the four calcareous soils and (0-6.40 P p.p.m.) for the brown soil and in the latter a range (0-28 P p.p.m.) was added.

In both procedures a ratio soil solution (1: 10) and an equilibrium time of 24 hours were used.

Each equilibrium stage was carried out in triplicate in order to avoid errors.

After the equilibrium was reached, the soil suspension was filtered through Whatman 42 paper and a suitable aliquot was taken up for the phosphorus analysis. This element was determined according to the Burriel Hernando method 1.947 (30).

The surface phosphorus determination was made according to the p patterns supplied by the Ernage Experimental Station.

The method adopted was:

A range of P^{31} added (1-4 P p.p.m.) in the form of a sodium diphosphate diluted solution, a ratio of soil: solution (1: 10), a certain amount of P^{32}, and equilibrium time of (8, 16, 24 and 48 hours).

The modus operandi was: In a 100 cc centrifugal tube, the solutions P^{31}, P^{32} and water were added and weighed; finally, 5 g. of soil - was introduced and the whole weighed.

After each equilibrium time, P^{32} was detected in a Geiger at Ernage Experimental Station and the P^{31} analysis was carried out according to the method of ammonium molybdate-stannouschloride widely used by the soil department at Gembloux University.

The surface P values were calculated according to the following equation:

$$e = (P_2 - P_1)\ ci \left[\frac{\dfrac{(P_3 - P_2)\ 548.389}{(P_2 - P_1)\ Ci}}{\dfrac{S/t}{(P_7 - P_8)\ Cf}} - 1 \right]$$

$$E = \frac{e}{P_5 - P_4} \times 100$$

E is expressed in P mg/100 g of soil.

In the above equation

P_1 = weight of centrifugal tube
P_2 = weight (Sol P^{31} + P_1)
P_3 = P_2 + weight of P^{32} solution
P_4 = P_3 + weight of water
P_5 = P_4 + 5 g. of soil
S = correction for disintegrations
t = time for the disintegrations
cf = P^{31} concentration in final solution (expressed in mg P)
Ci = P^{31} concentration added (expressed in mg P)

For all soils, it must be said that each equilibrium stage was carried out in quadruplicate.

Phosphorus desorption

1. 14 consecutive water extractions on the same soil sample

One of the laboratory procedures proposed by Fried et al. 1.956 (55) was followed.

This method consists of: 5 g. of soil sieved through 1 mm was placed in a 100 cc centrifugal tube, and 40 cc water was added. This soil - suspension was shaken about 1 hour and afterwards was centrifuged at - 4.000 r.p.m. during 1 hour. After this time the clear filtrate was collected. And again the same operation was repeated 14 times.

In all soils four replications were carried out.

The phosphorus in all extracts were analysed by Murphy and Riley's method as recommended by Van der Paaw-Sisingh in water extractions 1.968 1.971 (163) (1.964).

2. Soil-Water-Resin system

The Amer et al. procedure 1.955 (4) was followed; only a slight modification concerned with the type of resin was introduced. The Lawatit 600 Merck was used instead of the other types recommended by Amer et al., because in a previous study A. Campillo 1.971 (33) showed that this resin was the most efficient in relation to P adsorption.

The modus operandi was: In 125 cc erlenmeyer 1 g. of soil sieved - through 0.25 mm., 1 g. of Lewatit 600 (1-0.5 mm. size) saturated with Cl^- and 100 cc water were introduced. This erlenmeyer was placed on a shaker in a thermostatic chamber 20ºC + 0.5 and the system was shaken at a different equilibrium time (1, 2, 4, 5, 10, 20, 24, 48, 52 and 72 Hours) - continuously.

In all soils, for each equilibrium stage three replicates were carried out.

Once equilibrium was reached the anionic resin was removed from the soil suspension, through 0.3 mm sieving using a small portion of water.

This anionic resin was transferred carefully to an Aly column that is placed on a 100 cc volumetric flask, and then this anionic resin was slowly washed with 10 cc portions of sodium chloride (60 %) solution until a volume of 60 cc was collected in a volumetric flask. Afterwards, four water washing of 10 cc were made to the anionic resin and finally the volumetric flask was made up to 100 and well mixed. A 40 cc aliquot of this extract was taken up for the phosphorus analysis according to the Burriel Hernando method 1.947 (30).

3. Liberation of P adsorbed by soil

In order to have knowledge concerned with the behaviour of these soils in relation to their phosphorus transfer, the modus operandi followed was:

In 100 cc centrifugal tubes 2.5 g. of soil sieved through 1 mm. and 50 cc of a 0.01 M calcium chloride solution that contains 8 P p.p.m. ($Ca_2(H_2PO_4)$) were introduced. This soil suspension was shaken during 24 hours and later was centrifugated at 4.000 r.p.m. during 1 hour. This liquid was discarded and the soil residue underwent 14 consecutive extractions with water or 0.01 M calcium chloride solution; in each extraction, the equilibrium time being 1 hour and followed by a centrifugation at 4.000 r.p.m. and subsequent filtrate collection.

The phosphorus of these extracts was analysed by the Burriel Hernando method 1.947 (30).

Phosphorus dynamics and crop growth

In chapter 1, it was pointed out that we require to know what the behavious of these soils is like in relation to the phosphorus transfer and, as well, the influence of this nutrient on the crop growth and yield under the natural conditions of these soils. Thus, this implies the use of a biological procedure that supplies information related to the crop phosphorus yield, a consequence of its dry matter yield and phosphorus content.

1. Biological Assessments at Greenhouse

There are many biological procedures useful for this purpose; we followed one of them recommended by the soil department at Gembloux University; although this method is long assessment can amply satisfy these requirements.

This trial consists of: A cereal (rye-grass tetraploide gigantum), easily grown, was sown in 10 litre pots that contained a mixture in basis of volume formed by 80% washed sand (2 mm) and 20 of soil. These pots are perforated on their bottoms in order to carry out subirrigation in accordance with the following scheme:

An existing installation in one of the greenhouses at Aula Dei was used, assigned to the soil department. This intallation consists of 10 litre pots which are arranged in order to allow for automatic subirrigation through light pumping.

It must be borne in mind that the number of pots in this trial would be considerable; for ~~this reason~~, in this installation a previous test of subirrigation in these pots (with a mixing of sand and soil) was carried out. It could be verified that a down dragging of soil particles towards the water containers situated in the lower part of this installation was produced, although the pressure used in the pumping was light and the bottoms of these pots were covered with algodon and a piece of synthetic -

cloth (small mesh). Due to this difficulty, it was opted to irrigate on the surface of these pots, adding to each pot a 200 cc water amount twice a week; in this way we shall have the possibility of satisfying the water requirements by the crop and avoiding this dragging of soil particles.

On the other hand, the soil department belonging to the University of Gembloux recommended a nutritive solution whose anion/cation ratio was 0.97 and the concentration of this solution in a 50 litre volume will be:

NO_3^-	7,386 m.e.
$SO_4^=$	2,462 m.e.
K^+	3,563.4 m.e.
Ca^{++}	3,294.3 m.e.
Mg^{++}	3,294.3 m.e.

This solution will contain 100 cc of a microelement solution, which concentration will be as follows:

$Zn\ Cl_2$	4.73 g/litre
$Mn\ Cl_2$	10.00 g/litre
$H_3\ Bo_3$	15.00 g/litre
$Cu\ Cl_2.2H_2O$	1.33 g/litre
$Fe\ Cl_2.4H_2O$	45.86 g/litre
Ammonium molybdate	0.02 g/litre

As well, the staff of this soil department emphasized the chemical products to use and the suitable preparation of the above nutrient solution. These chemical reagents were Merck; for the cations (Ca, K and Mg) They were in the form of hydroxides and for the anions ($SO_4^=$ and NO_3^-) – they were respectively sulphuric and nitric acids in the amounts and volumes corresponding to the respective m.e. concentration cited above.

On the 1st of February 1.973, the biological assessment at the green house was initiated. This test consisted of a dosing of 6 replicates of –

pots with plants and 3 replicates of pots without plants for each soil. These pots had a mixture of 80 % sand and 20% soil in basis of volume, for that purpose a small container of known volume was used.

The soil volume was weighed before it was mixed with the sand; this handling took place in a large container; after that both materials were well homogenized by hand and were carefully introduced into the prepared pot.

On the 9th of February 1.973, 30 seeds of rye-grass tetraploide gigantum were drilled per pot; two days later the seedlings emerged and thinning was carried out, leaving 15 seedlings per pot.

The period of this assessment was until the completion of the growing cycle of this crop, for that purpose the above mentioned soil department recommended the supply of 600 m.e./pot of the above nutrient solution. During this time this trial was watched daily and the nutrient solution was ditributed as follows:

Age plant	m.e./pot	cc solution added/pot
2 days	20 m.e.	50
9 days	80 m.e.	200
23 days	100 m.e.	250
37 days	100 m.e.	250
51 days	100 m.e.	250
65 days	150 m.e.	375
79 days	150 m.e.	375

The above application was based on the crop growth and the criterion supported by Hanotiaux, in one of his papers (Hanotiaux 1.966 (75)).

At the end of this assessment, the plants from each pot were separately harvested, weighed, dried in an oven at t = 60ºC and weighed again. This plant material was well ground and well mixed. Two subsamples of 0.3

g. were digested with peroxide and sulphuric acid, such as is described by Van Schounwernburg 1.968 (165). The phosphorus of this extract was analysed according to the Murphy-Riley method such as is recommended by Van Schounwernburg 1.968 (165).

In the proceding greenhouse test, the no plants pots received the same nutrient solution application as the other pots. When the plants of the latter pots were harvested, the material from one of these pots was collected and left to dry at laboratory temperature. Once well dried, the whole of the material was passed through a 1 mm sieve in order to remove the sand particles added. The soil was well mixed and some subsamples were taken up for laboratory analysis.

In this trial (I), significant differences in phosphorus plant yield were found, for that reason we believe that it would be useful to verify this behaviour with a II assessment. For that purpose, on the 1st of May 1.973, rye-grass tetraploide gigantum was sown in the same pots before used in trial I and plants from each pot were harvested on the 15 th of July - 1.973. During the period of this II trial, the same conditions described before were followed; in other words, all that related to the use of nutrient solution, plant harvesting, weighing and phosphorus analysis, as - well as that concerned with the soil material from the no plants pots.

In the laboratory, these soil materials underwent the following extractions:

1. By 6N sulphuric acid solution, in the same way as was described before for total inorganic phosphorus (Hanotiaux's method).
2. By 2N sulphuric acid (Saunders and Williams procedure)
3. The fractionating sequence of Chang-Jackson until the phosphorus soluble in reductant.

The purpose of the above soil extractions was to compare, under the - same conditions, the plant phosphorus yield and the content of this element in soil. As well as to verify any alteration in these phosphorus soil frac tions. In fact, slightly higher values in phosphorus extracted by 2N and 6N sulphuric acid were found, and the increase of these values corresponded to the sum of the increase of the phosphorus extracted in the inorganic soil fractions; then we assumed that an alteration in the organic phosphorus had occured during the drying time at the laboratory or perhaps, at the greenhouse.

2. Laboratory procedures for assimilable phosphorus

On the other handm an estimation of assimilable phosphate was made according to the following procedures:

1) Burriel-Hornando method 1.950 (31)

This quick test is amply used in large numbers of Spanish laboratories. It consists of: an extracting solution based on:

1.0 g. calcium carbonate
0.9 g. magnesium carbonate
5 cc of sulphuric acid (20 %)
24.5 cc of acetic acid
Making up to 10 litres with water.

Extracting

2.5 g. soil sieved through 2 mm + 250 cc of the above solution were placed in a bottle and this soil suspension was shaken during 5 minutes; after that it was filtered through Whatman paper 42 and an appropriate aliquot was taken up for phosphorus analysis according to the procedure described by these authors (Burriel Hernando 1.947 (30)).

2) Olsen's method 1.953 (119)

This procedure was chosen because it is widely used as a quick test of phosphorus in calcareous soils. According to its authors, the action of this extracting solution is to diminish the calcium concentration in soil solution through calcium precipitation as calcium carbonate, resulting in an increase in the phosphorus concentration in this soil solution. On the other hand, in calcareous soils the secondary reactions of precipitation are reduced, due to the low calcium concentration in this extracting solution.

Modus operandi

Extraction

5 g. of soil + 100 cc (0.5 M Na HCO_3 solution buffered at pH 8.5) are placed in a 250 cc erlenmeyer and are shaken during 30 minutes. After that this soil suspension is filtered through Whatman paper 40. If the filtrate remained coloured, at teaspoon of carbon (free P) is added and it is - again shaken and filtered.

Colourmetric procedure

Reagents

1. Ammonium Molybdate solution.- 15 g. of ammonium molybdate are dissolved in 300 cc slightly hot water, left - to cool and 342 cc HCl are added, mixed well and made up to 1 litre. This solution must be kept in a dark flask.

2. Stannous chloride solution.- 10 g. of Cl_2 Sn. $2H_2O$ are dissolved in 25 cc of HCl and it is kept in a dark flask.

3. Stannous chloride diluted solution.- 0.75 cc from the above solution is diluted at 100 cc. This solution - must be prepared before using.

4.- Phosphorus solution.- 0.4393 g of K H_2PO_4 are dissolved in 1 litre water. This solution has 100 mg P/litre.

5. Phosphorus diluted solution.- 10 cc of the above solution is taken up and diluted to 250 cc with the extracting solution and kept in a dark flask. From this phosphorus diluted solution, 0, 1, 2, 3, 4 and 5 cc were taken up for the standard series.

Colour development

5 cc of soil extract is introduced into a 25 cc volumetric flask and 5 cc of ammonium molybdate solution is slowly added; await the CO_2 evolution and gently shake this flask and wash the neck of this flask with water to avoid the later direct contact of the solutions (1 and 3). Make up to 22 cc with water and finally add 1 cc of solution 3, mix well and make up to 25 cc and read at 10 minutes at 660 nk in the spectrophotocolourmeter.

Van der Paaw-Sissingh's procedure 1.968 (163), 1.971 (164)

This method was used because we had the experience that it reflects the phosphorus status well and therefore we required to evaluate it under these conditions.

It is characterized by a water extraction in an ample ratio of soil: water (1:60) in basis of volume and where the soil sample has been premoistened 24 hours before water extraction. Thus a certain volume of soil is placed in a 125 cc erlenmeyer and 2 cc water is added. This is mixed several times by hand shaking in order to moisten the soil sample well; after it is left to stand during 22 hours at t = 20º C.

Extraction

72 cc of water are added to this erlenmeyer and it is shaken during 1 hour. After, this soil suspension is filtered through a paper fixed well to the funnel to avoid a turbid filtrate.

Colourmetric determination

According to the Murphy and Riley method proposed by Van der Paaw - and Sissingh 1.971 (164).

Reagents

1. 5N sulphuric acid

2. 4 % ammonium molybdate solution

3. 1.75 % ascorbic acid solution

4. Potassium antimonium tartrate solution.- (0.275 g of $K_5b\ OC_4H_4O_6\ 1/2H_2O$ were dissolved in 100 cc water).

5. Mixed reagent.- In a 1 litre volumetric flask, mix 160 cc (nº 1), 50 cc (nº 2), 100 cc (nº 3) and 16 cc (nº 4) and make up to 1 litre with water.

6. Phosphorus solution.- 1.9617 g of KH_2PO_4 dissolved in 1 litre of water. This solution has 1.000 mg P_2O_5/litre. From this solution take the amounts corresponding to 10, 20, 40, 60, 80 mg P_2O_5/200 cc.

Colour development

20 cc of soil water extract and 20 cc of mixed reagent are introduced into a 100 cc erlenmeyer; both solutions are well mixed and the colour is read at 20 minutes at 720 nm in the spectrophotocolourmeter. The same is done for the blank and phosphorus standards.

CHAPTER 3

3.1. RESULTS AND DISCUSSION

3.2. PHYSICOCHEMICAL PROPERTIES OF THE SOIL IN RELATION TO THE PHOSPHORUS

3.3. DYNAMICS OF THE PHOSPHORUS IN THE SOIL AND GROWTH OF THE PLANTS

CHAPTER 3

In the introduction it was pointed out that a deeper knowledge of the phosphorus status in these soils would help us towards a better understainding of the problems that phosphorus fertilization involves.

For that reason, in this part 3.1. we shall study phosphorus distribution along the soil profile, total phosphorus organic and inorganic contents, fractions included in this total inorganic phosphorus, their contents and phosphorus compounds that contribute to the dominant inorganic fraction.

For that purpose we have subdivided this part in:

A) TOTAL PHOSPHORUS, ORGANIC AND INORGANIC

In its distribution along the soil profile in these five soils, estabihing with the figures obtained a comparison among them.

As a consequence of the difficulty that exists in the estimation of total organic phosphorus and given the fact that up to now all the laboratory procedures used and cited in the literature are indirect, we have chosen and used two laboratory methods for its evaluation as described previously.

B) INORGANIC PHOSPHORUS FRACTION

A well known laboratory method was followed that of Chang and Jackson, and its modification introduced by Hanotiaux 1.967 (40). The use of this laboratory procedure allowed us to know the contents of these inorganic phosphorus fractions as well as to verify the fact that these calcareous soils are slightly weathered.

C) PHOSPHORUS COMPOUNDS IN THE DOMINANT INORGANIC FRACTIONS

We estimate that the dominant fraction will be the phosphorus bound to calcium at hast for the calcareous soils; however we do not know which are the compounds for that reason, we have followed the criterion of Aslyng H.C. 1.964 (6).

3.1. RESULTS AND DISCUSSION

A) Total organic and inorganic phosphorus distribution along the soil profile

In table nº 13, the values of total phosphorus, organic and inorganic are included.

The total phosphorus content in the arable layer (Ap horizon) - shows higher values that range from 60.20 to 75.25 mgs P/100 g soil in 3 calcareous soils (gypsum serosem, terrace soil and alluvial meadow soil from the River Gállego), an intermediate value 38.70 mg P/100 g for Brown soil and the Lowest content of 28.60 mg. P/100 g soil for the marly serosem.

The total phosphorus distribution along the soil profile is different in these soils studied, for two calcareous soils (gypsum serosem and terrace soil) it decreased gradually from relatively higher values to very low ares according to soil depth (60.2 to 17.8 and from 75.3 to 23.3); while in the other calcareous soils (alluvial meadow soil from the river Gállego and marly serosem) this decreasing related to the depth is less pronunced (70.9 to 41.8 and 28.60 to 21.60) respectevely. In Brown soil, the total phosphorus content in the Ap horizon is similar to that of the deepest horizons (Bvcv) and the Bv horizon showed a slightly lower content - than those of these horizons mentioned.

The above mentioned total phosphorus distribution is different in these five soils and it induce us to believe that it can be inlfuenced by the organic phosphorus content in the soil horizons. Coming back to table nº 13, it can be observed that the organic phosphorus obtained for both laboratory procedures shows a similar tendency in its distribution that corresponds to that mentioned for the total phosphorus in these five soils.

This organic phosphorus distribution in two calcareous soils (gypsum serosem and terrace soil) follows a similar pattern to that exhibited by the organic matter, proper to the mineral soils in which drainage conditions are excellent, while in the other two soils (maral serosem and alluvial meadow soil from Gallego River) this organic phosphorus distribution was slightly decreased along the different horizons, showing that there is a slight impediment in drainage conditions. These facts are in accordance with what has been reported by Kaila 1.963 (88, 89) Williams E.G. and W.M.H. Saunders 1.956 (172); Hoyos and García 1.963 (82).

In Brown soil, this organic phosphorus content in its different horizons and estimated by both laboratory procedures, is related to the organic matter distribution in these soil horizons. So we can deduce that the organic matter content in the deepest horizon (Bvcv) was originated from a certain baching of the organic matter from the upper horizons and a certain accumulation of roots residues of the coniferous vegetation established in this soil.

On the other hand, the figures of organic phosphorus in these five soils obtained by both laboratory methods, are quite different; that can be seen in the same table.

It has been previously mentioned that these two laboratory methods as well as all those cited in the literature, estimate the total organic phosphorus indirectly that is to say as the differences between the total phosphorus and the inorganic. In the case of the Saunders-Williams procedure 1.955 (139), the total phosphorus is reflected by the amount of phos phorus obtained in the sulphuric extraction of a soil sample previously incinerated at 500ºC during 1 hour; while in Hanotiaux's method (76) that equals the phosphorus extracted from a soil sample digested with percloric acid.

For both laboratory methods, total inorganic phosphorus is equal to that extracted in a soil sample by 2N and 6N sulphuric acid respectively.

These values can be seen in table nº 13 and they are similar for both methods. Then the difference between the values of organic phosphorus estimated by both laboratory procedure can be for the following reasons:

1. The incineration of the soil sample at 500ºC during 1 hour does not produces a complete destruction of organic matter or it can produce a refixation of the mineralized phosphorus as consequence of these high temperature as it was pointed out by Kaila for some Finland soils.

These facts can be conducted to have a lower value than that obtained in a soil sample digested with percloric acid.

2. That in the organic phosphorus values calculated by the Hanotiaux procedure, some inorganic phosphorus fractions resistent to extraction are included. That can be the case of some soils where the values of 6N sulphuric acid are lower to the sum of the all P inorganic fractions.

All this complicates the choice both laboratory procedure because:

1. The Saunders-Williams method has been considered by several scientists (Kaila 1.963 (88); Enwezoor 1.966 (49)) as a standard method in organic phosphorus soils studies because it supplies the highest values in this form of phosphorus.

In these soils the values of organic phosphorus obtained by this method were in the range (206 to 86 p.p.m. P) similar to those reported - by Greb B.W. - Olsen 1.967 (64) for the colorado calcareous soils and by Pratt P.F. 1.963 (130 b) for the California alluvial and lake soils.

2. In relation to this procedure of Hanotiaux there can be included some inorganic phosphorus fractions resistent to the extraction in its organic phosphorus value. A comparison between the values of inorganic phosphorus obtained by 6N sulphuric extraction and the summ of all these inorganic P fraction was taken account.

Thus, if this criterion is applied, we can say that the values of organic phosphorus obtained by Hanotiaux procedure are suitable in all cases except in the case of Maral serosem which shows higher values of the summ all inorganic P fractions than those extracted by 6N sulphuric acid. However in this study an organic phosphorus fractioning was not carried out that means that we can not study more deeply the efficacy of both laboratory procedures for our soils, and for that reason we believe that a detailed study related to this subject will be welcome.

Some soil workers (Black and Goring 1.953 (19); Enwezoor 1.967 (46); Kaila 1.963 (86)) have used a similar ratio to the C/N for organic matter mineralization, consisting of the organic carbon/organic phosphorus ratio for that of the organic phosphorus, when this ratio is lower than 200 mineralization takes place and at higher values than 200, the situation is inverse. However A. Van Diest 1.968 (162) points out that phosphorus inmobilization can occur when the OC/OP ratio is higher than 100.

In all soil horizons both procedures shows a OC/OP ratio lower than 100 and then there is a mineralization situation.

Table nº 13.- Total organic and inorganic phosphorus in soil horizons. These values are expressed in (mg P/100 g. soil).

Soils	Depth (cms)	Horizon	Total P	% O.M.	% O.C.	Saunders - Williams		Hanotiaux		OC/OP	
						Org P	Mineral P	Org P	Mineral P	Saunders-Williams	Hanotiaux
Gypsum serosem	0- 50	Ap	60.20	2.120	1.23	20.60	24.10	38.70	21.50	59.7	31.8
	50- 80	Ah_2	47.30	1.448	0.84	17.20	19.40	28.90	18.40	48.0	28.4
	80-115	Cl_y	43.00	0.586	0.34	9.68	17.20	25.80	17.20	40.0	13.0
	+ 115	C2	17.80	0.155	0.09	2.20	12.90	2.30	13.80	10.0	45.0
Maral serosem	0- 45	Ap	28.60	1.137	0.66	8.60	15.01	13.10	15.50	76.0	50.40
	45- 62	Ab_2	21.50	0.761	0.44	7.31	10.39	9.80	12.00	61.0	46.30
	62- 80	Bp	21.60	0.482	0.28	4.30	12.04	10.40	11.20	65.0	26.90
	80-100	D_1	21.60	0.362	0.21	2.58	11.61	10.00	8.60	8.9	24.80
Terrace soil	0- 42	Ap	75.25	1.413	0.82	18.30	39.77	33.77	41.28	42.0	24.90
	42- 55	Bv	36.55	0.896	0.52	10.50	14.62	22.91	14.64	49.0	22.90
	+ 55	CCa	23.31	0.672	0.39	11.90	9.03	12.83	10.48	33.0	30.00
Alluvial meadow soil	0- 40	Ap	70.95	1.520	0.88	19.61	37.88	30.55	40.40	45.0	30.00
	40-110	B	40.29	0.670	0.39	5.38	19.11	22.15	18.10	72.0	17.70
	110-120	M_1	42.30	0.520	0.30	7.24	18.53	23.40	18.90	40.0	12.80
	+ 120	M_2	41.80	0.530	0.31	8.38	19.35	22.45	17.20	37.0	13.50
Brown soil	0- 45	Ap	38.70	1.390	0.81	11.45	15.90	21.50	17.20	70.0	39.00
	45- 90	Bv	28.84	0.670	0.39	6.97	11.40	17.66	11.18	55.0	22.00
	90-110	Bvcv	31.06	0.89	0.52	6.98	8.12	23.32	7.74	74.0	22.00

B) Fractions of total inorganic phosphorus.-

In tables 14,15,16,17 and 18 the values obtained for the different inorganic phosphorus fractions which constitute the total inorganic phosphorus, following the original procedure of Chang-Jackson 1957 (32) and its modification introduced by Hanatiaux 1964 (70), have been included. The purpose of using this modification was to verify the estimation of the phosphorus soluble in 0.5 N ammonium fluoride; on the basis of the figures obtained we can say that this estimation was similar in four calcareous soils with the two laboratory procedures; although for the brown soil (table 18) it was slightly higher with Hanatiaux's modification and the use of this 0.5 N ammonium fluoride solution buffered at 8.5 pH influenced the later extraction of the phosphorus soluble in 0.1 N sodium hydroxide; for that reason it was deduced that this Hanatiaux's modification is valid when we require to know all inorganic phosphorus fractions in non calcareous soil.

Even with regard to the occluded forms the original method of Chang-Jackson was followed, and on this soil residue two consecutive 0.5 N sulphuric acid extractions were carried out, in order to know if this original method of Chang-Jackson extracted all the occluded phosphorus. The results obtained show that:

In the two extractions carried out calcium phosphorus continues being extracted.

The values obtained were low if they are compared with other inorganic phosphorus fractions; however, with the preceding they are higher since in the majority of cases they furnish approximately 100% of the value considered.

In the four calcarenous soils, according to the results obtained in the inorganic P fractions, the dominant fraction was the P Ca, afterwards the P soluble in reductant, and the other solubles in ammonium chloride and ammonium fluoride were low.

In the occluded folrms, for all these soil horizons, only the P Ca was detected.

In brown soil, the P soluble in reductant showed the highest value in all its horizons. As was mentioned before for this soil, the original method of Chang-Jackson and the modification introduced by Hanatiaux, furnish slightly higher values in P soluble in ammonium fluoride than this - original method; besides it influenced the P soluble in 0.1 N sodium hydroxide.

It can be said that according to the modification of Hanatiaux, in the Ap horizon the values of P soluble in 0.1 sodium hydroxide, in 0.5 - ammonium fluoride and 0.5 N sulphuric acid were similar, while in the deepest horizon (Bvcv) the P Ca decreased.

It can be considered that this P Ca fraction is included in the - coarser soil particles and the P Al and P Fa in the silt and clay particles. Thiscan be supported by the findings of Hanley P.K. and M.D. Murphy 1970 (72) for soils similar to the brown soil.

On the other hand, this brown soil had lower values in occluded - p forms.

Table nº 14.- Inorganic phosphorus fractions in gypsum serosem. This data is expressed (in mg P/100 g soil)

1) Original Chang-Jackson method

Fractions	Soil - horizons			
	Ap	Ah_2	C_1y	C_2
P-$ClNH_4$ (pH 7.0)	0.96	0.34	0.34	0.50
P-NH_4F (pH 8.2)	0.75	0.00	0.00	0.54
P-Na OH 0,1N	0.08	0.00	0.00	0.00
P-H_2SO_4 0.5N	14.00	13.40	9.68	10.40
P in reductant occluded forms	6.73	6.23	5.59	2.15
P - Al	0.00	0.00	0.00	0.00
P - Fe	0.00	0.00	0.00	0.00
P - Ca	1.29	2.00	2.60	2.60
+P - Ca	0.43	1.80	3.00	2.00
+P - Ca	0.43	0.40	0.40	0.40
sum	25.68	24.11	20.54	16.59

2) Modification introduced by Hanatiaux.-

Fractions	Ap	Ah_2	C_1y	C_2
P-$ClNH_4$ 1N	0.65	0.16	0.19	0.46
P-NH_4F (pH 8.5)	0.43	0.00	0.00	0.00
P-NaOH 0.1N	0.00	0.00	0.00	0.00
P-H_2SO_4 0.5N	12.00	12.00	8.45	8.95
P in reductant occluded forms	10.02	6.88	4.73	3.87
P - Al	0.00	0.00	0.00	0.00
P - Fe	0.00	0.00	0.00	0.00
Sum	23.10	18.04	13.37	13.28

Table nº 15.- Inorganic phosphorus fractions in marly serosem. This data is expressed (in mg P/100 g soil)

1) Original Chang-Jackson method

Fractions	Soil - horizons			
	Ap	Ah_2	Bp	D_1
P - $ClNH_4$ (pH 7)	0.73	0.13	0.00	0.13
P - NH_4F (pH 8.2)	1.79	1.49	0.53	0.00
P - NaOH 0.1N	0.00	0.00	0.00	0.00
P - H_2SO_4 0.5N	10.00	9.64	10.68	10.40
P in reductant occluded forms	4.73	4.73	5.20	2.00
P - Al	1.25	1.00	0.00	0.00
P - Fe	0.00	0.00	0.00	0.00
P - Ca	2.00	3.00	2.00	2.00
+ P - Ca	0.43	1.20	2.00	2.00
+ P - Ca	0.11	0.40	0.40	0.40
Sum	21.04	20.59	20.81	16.93

2) Modification introduced by Hanotiaux

P - $ClNH_4$	0.77	0.00	0.00	0.00
P - NH_4F (pH 8.5)	1.83	2.04	0.86	0.00
P - NaOH 0.1N	0.00	0.00	0.00	0.00
P - H_2SO_4 0.5N	10.00	10.00	8.05	9.95
P in reductant occluded forms	6.45	5.79	6.45	2.59
P - Al	1.00	0.70	0.00	0.00
P - Fe	0.00	0.00	0.00	0.00
Sum	20.05	18.53	15.36	12.62

Table nº 16.- Inorganic phosphorus fractions in terrace soil. This data is expressed (in mg P/100 g soil)

1) Original Chang-Janckson method

Fractions	Soil - horizons		
	Ap	Bv	C Ca
P - $ClNH_4$	1.10	0.21	0.34
P - NH_4F (pH 8.2)	2.28	0.21	0.33
P - NaOH 0.1N	0.04	0.00	0.00
P - H_2SO_4 0.5N	18.11	7.09	5.16
P in reductant occluded forms	7.10	2.58	2.58
P - Al	0.50	0.00	0.00
P - Fe	0.00	0.00	0.00
P - Ca	2.00	2.00	2.00
+ P - Ca	1.29	1.00	1.50
+ P - Ca	0.43	1.00	0.50
Sum	33.02	14.09	11.41

2) Modification introduced by Hanotiaux

P - $ClNH_4$	1.26	0.13	0.13
P - NH_4F (pH 8.5)	2.37	0.00	0.44
P - NaOH 0.1N	0.00	0.00	0.00
P - H_2SO_4 0.5N	16.69	5.85	4.85
P in reductant occluded forms	7.74	6.24	6.24
P - Al	0.75	0.00	0.00
P - Fe	0.00	0.00	0.00
Sum	28.81	12.22	11.66

Table nº 17.- Inorganic phosphorus fractions in alluvial meadow soil from the River Gállego. This data is expressed (in mg P/100 g soil).

1) Original Chang-Jackson method

Fractions	Soil - horizons			
	Ap	B	M_1	M_2
P - $ClNH_4$ (pH 7.0)	1.34	0.26	0.38	0.13
P - NH_4F (pH 8.2)	3.23	0.00	0.53	0.00
P - NaOH 0.1N	0.08	0.00	0.00	0.00
P - H_2SO_4 0.5N	20.12	7.10	8.40	7.00
P in reductant occluded forms	7.00	5.80	5.37	2.58
P - Al	0.00	0.00	0.00	0.00
P - Fe	0.00	0.00	0.00	0.00
P - Ca	2.00	1.50	1.80	1.60
+ P - Ca	1.40	1.00	1.00	1.00
+ P - Ca	1.00	1.00	1.00	1.00
Sum	37.02	16.66	18.73	13.11

2) Modification introduced by Hanotiaux

P - $ClNH_4$	1.93	0.00	0.17	0.13
P - NH_4F (pH 8.5)	2.55	0.43	0.00	0.00
P - NaOH 0.1N	0.00	0.00	0.00	0.00
P - H_2SO_4 0.5N	22.38	6.98	10.00	6.45
P in reductant occluded forms	8.03	7.74	3.87	3.87
P - Al	1.00	0.00	0.00	0.00
P - Fe	0.00	0.00	0.00	0.00
Sum	35.89	15.15	14.04	10.65

Table nº 18.- Inorganic phosphorus fractions in brown soil. This data is expressed (in mg P/100 g soil)

1) Original Chang-Jackson method

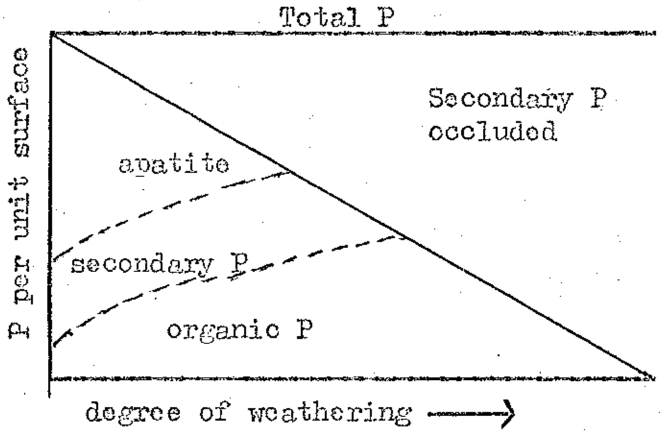
Fractions	Soil - horizons Ap	 Bv	 Bvcv
P - $ClNH_4$	0.17	0.13	0.34
P - NH_4F (pH 8.2)	1.60	0.45	0.00
P - NaOH 0.1N	0.27	0.36	0.21
P - H_2SO_4 0.5N	3.80	3.54	0.43
P in reductant occluded forms	11.40	10.00	10.00
P - Al	0.70	0.50	0.00
P - Fe	0.15	0.15	0.15
P - Ca	0.43	0.20	0.20
‡ P - Ca	0.15	0.20	0.10
+ P - Ca	0.05	0.00	0.10
Sum	18.69	15.53	11.53

2) Modification introduced by Hanotiaux

Fractions	Ap	Bv	Bvcv
P - $ClNH_4$	0.17	0.00	0.00
P - NH_4F (pH 8.5)	3.10	0.43	0.30
P - NaOH 0.1N	2.32	0.95	0.64
P - H_2SO_4 0.5N	3.87	1.63	0.00
P in reductant occluded forms	10.40	9.80	10.00
P - Al	0.60	0.50	0.00
P - Fe	0.00	0.00	0.00
Sum	20.46	13.31	10.94

How can we explain that in a soil there are different inorganic P forms and these have different contents if in all cases they have come from an apatite compound found in rocks ?

In order to clarify this situation, let us consider the scheme proposed by Williams and Walker 1.969 (176).



The difference between a rock residue and a soil is that in the latter there exists life, expressed by the presence of microorganisms. These attack the apatite (only mineralogical P form existing) by means of segregation of organic acids such as: oxalic, glycolic, acetic, etc., that produce the P solubilization form t is mineral. These soil microorganisms take part of this liberated P according to their needs and incorporate it in their organism; in this way, it was transformed in organic form. Another portion of this liberated P reacts with the soil constituyents and originates the formation of secondary phosphates. This is a dynamic process, some of the soil microorganisms dying and again the P is incorporated in the soil and reacts with secondary phosphates.

In weathered soils, where iron and alumina oxides and hydroxides and acid clays exist, part of the secondary phosphates, that proceeding from the reactions with soil and, as well, that coming from the organic P mineralization, will remain coated by these iron oxides-hydroxides or included, forming a part of the crystaline structure and then occluded P appears. In order to have this situation, it is necessary the -

intervention of several factors such as: time, temperature, precipitation, microbiological activity, etc. In such a way, the presence of inorganic phosphorus fractions in soils was concerned, and recently the soil department of Illinois University (Smeck N.E. 1.973 (173)) has considered that water and organic matter are intensity factors, and among the capacity factors phosphorus forms along the soil profile, is one of these main capacity factors when one tries to know the degree of weathering of a soil (Runge 1.973 (136)).

With this purpose this inorganic phosphorus distribution along the soil profile will be considered in the 7th soils classification in order to distinguish and to be more precise about the great soil groups. (Hinkley et al. 1.970 (81)).

If we apply the criterion of (Black C.A. and Whitney 1.966 (20), Chang S.C. and Jackson M.L. 1.958 (35), Dannke W.C. et al. 1.964 (42), Hawkins R.M. and G.W. kunze 1.965 (79), Hsu P.H. and M.L. Jackson 1.960 (83), Runge E.C.A. and F.F. Rucken 1.966 (135)) and express these values of inorganic phosphorus fractions (tables 14, 15, 16, 17, and 18) as the percentage of total inorganic phosphorus in a graph, it will be possible to know the degree of weathering in these soils.

From graph 1 it can be deduced that the four calcareous soils show a slight to moderate degree of weathering that agrees with the idea that we have of them; that they are young soils in which leaching is scarce due to a precipitation of 350 mm per annum.

In relation to the brown soil, formed in a previous geologic period and where there has been a precipitation to produce the leaching of bases, it can be observed that the degree of weathering is higher. That fact agrees with that found by Madlyn 1.961 (108) in leached brown soil developed from morrena type parent material.

C) P compounds in the dominant inorganic phosphorus fraction.

It has been seen that in the four calcareous soils, this inorganic P fraction wes the one bound to calcium and in the Ap horizon of brown soil the content of P-Ca was similar to those corresponding to P-Al and P-Fe. Therefore, we require to know which compounds are included in this fraction. Using the lime and phosphate potentials in the same way as is reported by Aslyng 1964 (6), we shall be able to deduce the nature of these compounds. So we have calculated these potentials as follows:

$$\text{lime potential} = \text{pH} - 1/2 \text{ p Ca}$$

$$\text{phosphate potential} = 1/2 \text{ p Ca} + \text{p } H_2 \, PO_4$$

Following Aslyng's method described beforehand, the calcium concentration in final solution was similar to that added. For that reason the initial calcium concentration was used to calculate the ionic strength, activity coefficients and phosphate potential.

$$1/2 \text{ p Ca} = - 1/2 \, (\log \text{Con}_{\text{Calcium}} + \log f)$$

$$\log f = \frac{A Z^2 \sqrt{\mu}}{1 + aB \sqrt{\mu}}$$

where

A = 0.5

n = ionic strength

aB = 1.5

Z = ionic valency

For a 0.01 M calcium chloride solution, 1/2 p Ca = 1.173 (according to above equation).

$$P \, H_2 \, PO_4 = - (\log \text{con}_{H_2 \, PO_4} + \log f)$$

$$\log \text{con}_{H_2 \, PO_4} = p \, (p) + (p \, \frac{H}{K'' + H})$$

$p\left(\frac{H}{K'' + H}\right)$ is a correction factor calculated by Aslyng 1964 (6).
This factor relates $\frac{H_2\ PO_4^{-}}{P}$ to pH.

The phosphate potential ($1/2\ p\ Ca + P\ H_2\ PO_4$) increases when the product of the active ions decreases. Therefore, Larsen L. (1.965) (100) reported that when the soil pH is higher than 6, the phosphate potential must be corrected, taking into account the formation of the complex.

$$Ca^{2+} + H\ PO_4^{2-} \rightleftharpoons Ca\ H\ PO_4$$

For that reason, the equation was transformated into:

$$(P) = (H_2\ PO_4) + (\ H_2\ PO_4)\ x\ 10^{PH-pK} + 2\ (H_2\ PO_4)\ (Ca)\ (10^{pH-pKc-pK_2}$$

p Kc = 2 according to Grenwald 1960 (65)
$p\ K_2$ = 7 according to Bjenum and Unmark 1919 (18)

In table 19, the lime and phosphate potentiales are included.

Afterwards, these values were compared with the plottings of knom calcium phosphate compounds, such as can be seen in graph 2 and they fell between the lines of the hydroxiapatite and octacalcium phosphate for the five soils studied.

Graph 1

INORGANIC PHOSPHORUS FRACTION

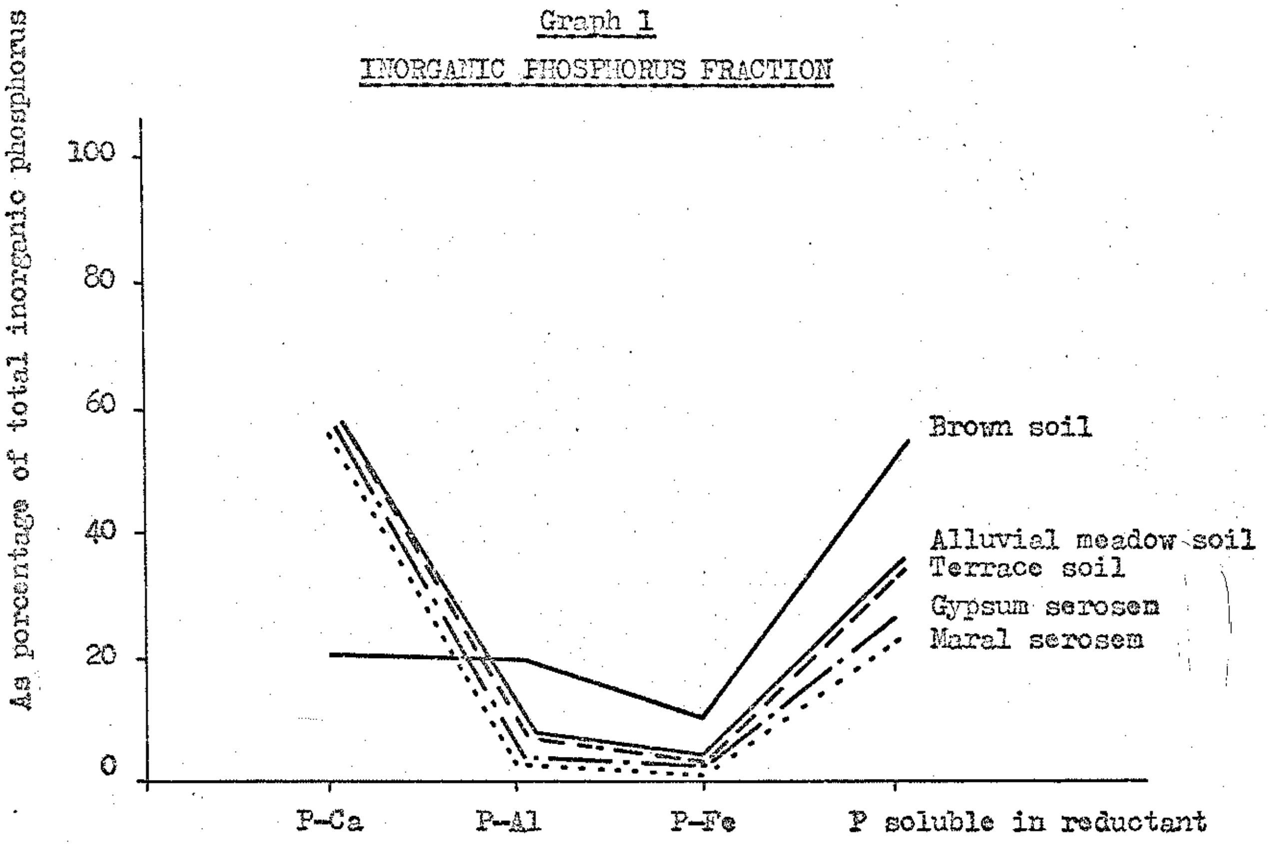
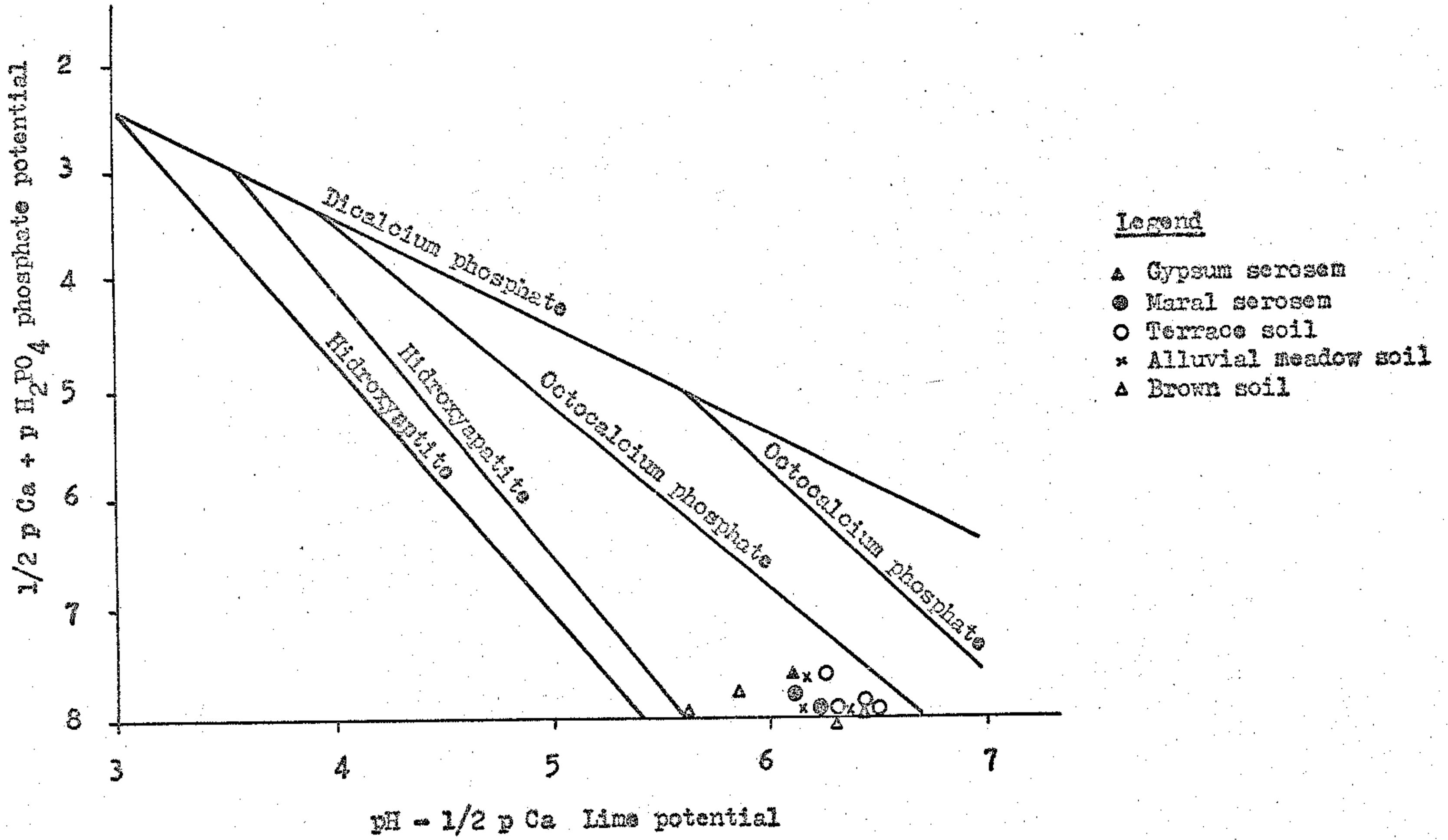


Table nº 19.- Phosphate and lime Potentials.

Soils	Depth (cm)	Horizon	pH	In p.p.m.p. Phosphorus concentration	Potentials		
					Lime (pH-1/2pCa)	Phos-phate	(1/2pCa+pH_2PO_4)
Gypsum serosem	0.50	Ap	7.30	0.0290	6.13	7.69	7.92 +
	50.80	Ah2	7.50	0.0160	6.33	8.09	8.34
	80-115	C1y	7.60	0.0160	6.43	8.17	8.38
	+ 115	C2	7.60	0.0150	6.43	8.17	8.38
Marly serosem	0-45	Ap	7.36	0.0215	6.19	7.85	8.19
	45-62	Ah2	7.45	0.0160	6.26	7.93	8.29
	62-80	Bp	7.55	0.0160	6.38	8.09	8.34
	80-100	D1	7.60	0.0150	6.43	8.17	8.38
Terrace soil	0-42	Ap	7.30	0.0290	6.13	7.69	7.92
	42-55	Bv	7.45	0.0160	6.26	7.93	8.29
	+ 55	Cca	7.50	0.0150	6.38	8.09	8.34
Alluvial meadow soil from River Gállego	0-40	Ap	7.45	0.0430	6.28	7.63	7.87
	40-110	B	7.50	0.0220	6.33	7.95	8.20
	110-120	M1	7.60	0.0180	6.43	8.02	8.38
	+ 55	M2	7.60	0.0160	6.43	8.17	8.38
Brown soil	0.45	Ap	7.12	0.0215	5.95	7.74	7.91
	45-90	Bv	7.12	0.0150	5.63	7.79	8.07
	90-110	Bvcv	7.12	0.0150	5.63	7.71	8.07

+ corrected values according to the criterion of Larsen.

Graph 2


1/2 p Ca + p H_2PO_4 phosphate potential
2
3
4
5
6
7
8
3
4
5
6
7
pH - 1/2 p Ca Lime potential
Dicalcium phosphate
Octocalcium phosphate
Octocalcium phosphate
Hidroxyapatite
Hidroxyapatite
Legend
▲ Gypsum serosem
● Maral serosem
○ Terrace soil
× Alluvial meadow soil
△ Brown soil

3.2. PHYSICOCHEMICAL PROPERTIES OF THE SOIL IN RELATION TO THE PHOSPHORUS

A) Phosphorus adsorption

In the introduction to this study, what is known as adsorption was defined and, as well, the theories concerned with the mechanics by which -it is produced in the soil constituents (calcium carbonate and clay-calcium) were pointed out, intuiting that in calcareous soils there exist both mechanics together. For the quantitative evaluation of this process, the soil workers have used isotherme, reflecting in this way the different patterns shown by soils. In order to achieve this purpose, in chapter 2, methodology, two laboratory procedures wers described, one of them with the use of diluted potassium diphosphate solutions buffered at pH 7.0 and the other with increased amounts of calcium diphosphate in a 0.01 M Calcium Chloride medium. In both cases, the soil: solution ratio was 1:20 and equilibrium time was 24 hours. The phosphorus in the final solution was analysed by the Burriel-Hernando method.

We have used these two laboratory procedures for the following purposes:

1) As has been mentioned before, it is the first time that a study of phosphorus adsortion has been carried out, therefore, we require to know what the estimation of this process by both laboratory procedures is like.-

2) In order to be precise about the buffering capacity factor according to the criterion of the Australian soil workers (Ozanne et al 1968) (120) who use the calcium diphosphate in a 0.01 M calcium chloride medium.-

We must point out that in the adsorption and desorption phosphorus studies, the Ap horizon of all soils was used.

Superficial phosphorus

When we require to know the total maximum P adsorption by a soil, it is necessary to take into account the P superficial content of a soil,- otherwise in soils that have a high content in this phosphorus form, if this value is not included in the data of P sorption, it will produce an unsuitable estimation of the total maximum phosphorus adsorption. (Fried et al 1967 (57), Olsen and Watanabe 1957 (122).-

Following this criterion a phosphorus superficial determination was made according to a laboratory procedure proposed by the Ernage - Experimental Station (Belgium).-

This data of surface phosphorus is included in table 20.

TABLE 20

Phosphorus surface values expressed (in mg P/100 g soil) according to equilibrium time and P^{31} added.-

Soils	Equilibrium time in hours	p^{31} added in P p.p.m.			
		1	2	3	4
Gypsum serosem	8	2.13	2.13	2.00	2.00
	16	2.43	2.50	2.50	2.50
	24	2.50	2.50	3.00	2.40
	48	2.50	2.50	2.50	2.50
Marly serosem	8	3.70	3.80	3.95	3.95
	16	3.87	3.96	3.80	3.80
	24	4.00	4.00	4.00	4.00
	48	4.00	4.00	4.00	4.00
Terrace soil	8	3.63	4.60	3.40	4.10
	16	4.40	4.40	4.30	4.30
	24	3.50	4.40	4.30	4.30
	48	3.60	3.60	4.60	4.60

(continuation of Table 20)

Soils	Equilibrium time in hours	P^{31} added in P p.p.m.			
		1	2	3	4
Alluvial meadow soil from River Gállego	8	3.00	5.00	2.98	3.55
	16	5.40	6.30	8.00	6.20
	24	7.13	7.00	7.00	7.00
	48	6.80	7.00	7.00	7.00
Brown soil	8	1.40	1.80	1.60	1.60
	16	1.60	1.90	2.10	1.70
	24	1.60	1.50	1.70	1.60
	48	1.60	1.60	1.60	1.60

The choice of the suitable value for the surface phosphorus was difficult due to certain different features of these soils, which means that the equilibrium is not reached at the same time. So for gypsum serosem and terrace soil it was at 16 hours while for the rest of the soils it was at 24 hours.

This phosphorus surface data is:

Soils	Surface P (in P p.p.m.)
Gysum serosem	25.00
Marly serosem	40.00
Terrace soil	43.00
Alluvial meadow soil from River Gállego	70.00
Brown soil	16.00

1. Method of potassium diphosphate diluted solutions buffered at pH 7.0

The data of phosphorus sorption according to this procedure can be seen in table 21. In this table can be seen the initial P concentration added, the final obtained after equilibrium time; the P sorption values calculated as the difference between the initial concentration minus the final divided by 5 as the soil: solution ratio was (1:20) and, finally, the last column reflects this difference /5 + the P surface.

TABLE 21

Phosphorus sorbed by soil expressed in p.p.m.P. According to the $K_2H_2PO_4$ method.

Soils	P Concentration expressed in g P/100 cc			P sorbed by soil (in p.p.m.P)	
	Initial	Final	Difference	Difference/5	Difference/5 + Surface P
Gypsum serosem	200	19.6	180.4	36.1	61.1
	300	38.7	261.3	52.2	77.2
	400	91.0	300.0	61.0	86.0
	800	290.0	510.0	102.0	127.0
	1200	562.0	638.0	127.0	152.0
	1600	774.0	826.0	165.0	190.0
	2000	1032.0	968.0	194.0	219.0
	2400	1354.0	1046.0	209.0	234.0
	2800	1612.0	1188.0	238.0	263.0
	3200	1906.0	1294.0	258.0	283.0
	3600	2064.0	1536.0	307.0	332.0
	4000	2406.0	1592.0	318.0	343.0
Marly serosem	200	25.8	174.2	34.8	74.8
	300	80.0	220.0	44.0	84.0
	400	175.0	225.0	45.0	85.0
	800	398.0	402.0	80.4	120.4
	1200	709.0	491.0	98.2	138.2
	1600	1010.0	590.0	118.2	158.0
	2000	1333.0	667.0	133.0	173.0
	2400	1720.0	680.0	136.0	176.0
	2800	1956.0	844.0	168.8	208.8
	3200	2322.0	878.0	175.4	215.1
	3600	2666.0	934.0	186.8	226.8
	4000	3064.0	936.0	187.2	227.2

(continuation of Table 21)

Soils	P Concentration expressed in g P/100 cc			P sorbed by soil (in p.p.m.P)	
	Initial	Final	Difference	Difference/5	Difference/5 + Surface P
Terrace soil	200	53,8	146,2	29.2	72.2
	300	151.0	149.0	29.0	72.4
	400	265.0	135.0	27.0	70.0
	800	483.0	317.0	63.0	106.0
	1200	795.0	405.0	81.0	124.0
	1600	1075.0	525.0	105.0	148.0
	2000	1440.0	560.0	112.0	155.0
	2400	1795.0	605.0	121.0	164.0
	2800	2128.0	672.0	134.0	177.0
	3200	2494.0	706.0	141.0	184.0
	3600	2838.0	762.0	152.0	195.0
	4000	3182.0	818.0	163.0	206.0
Alluvial meadow soil from River Gállego	200	43.0	157.0	31.4	101.4
	300	125.0	175.0	35.0	105.0
	400	165.0	235.0	47.0	117.0
	800	379.0	421.0	84.0	154.0
	1200	685.0	515.0	104.0	173.0
	1600	934.0	666.0	133.0	203.0
	2000	1161.0	839.0	168.0	238.0
	2400	1440.0	860.0	172.0	242.0
	2800	1849.0	931.0	190.0	260.0
	3200	2264.0	936.0	188.0	258.0
	3600	2643.0	957.0	191.0	261.0
	4000	3010.0	990.0	198.0	268.0
Brown soil	80	15.3	64.70	12.94	28.94
	160	41.9	118.10	23.60	39.64
	240	88.2	151.80	30.60	46.60
	320	146.0	174.00	35.00	51.00
	400	184.9	215.10	43.00	59.00
	480	222.0	258.0	51.00	68.00
	560	279.0	281.0	56.00	72.00
	640	355.0	295.0	59.00	75.00

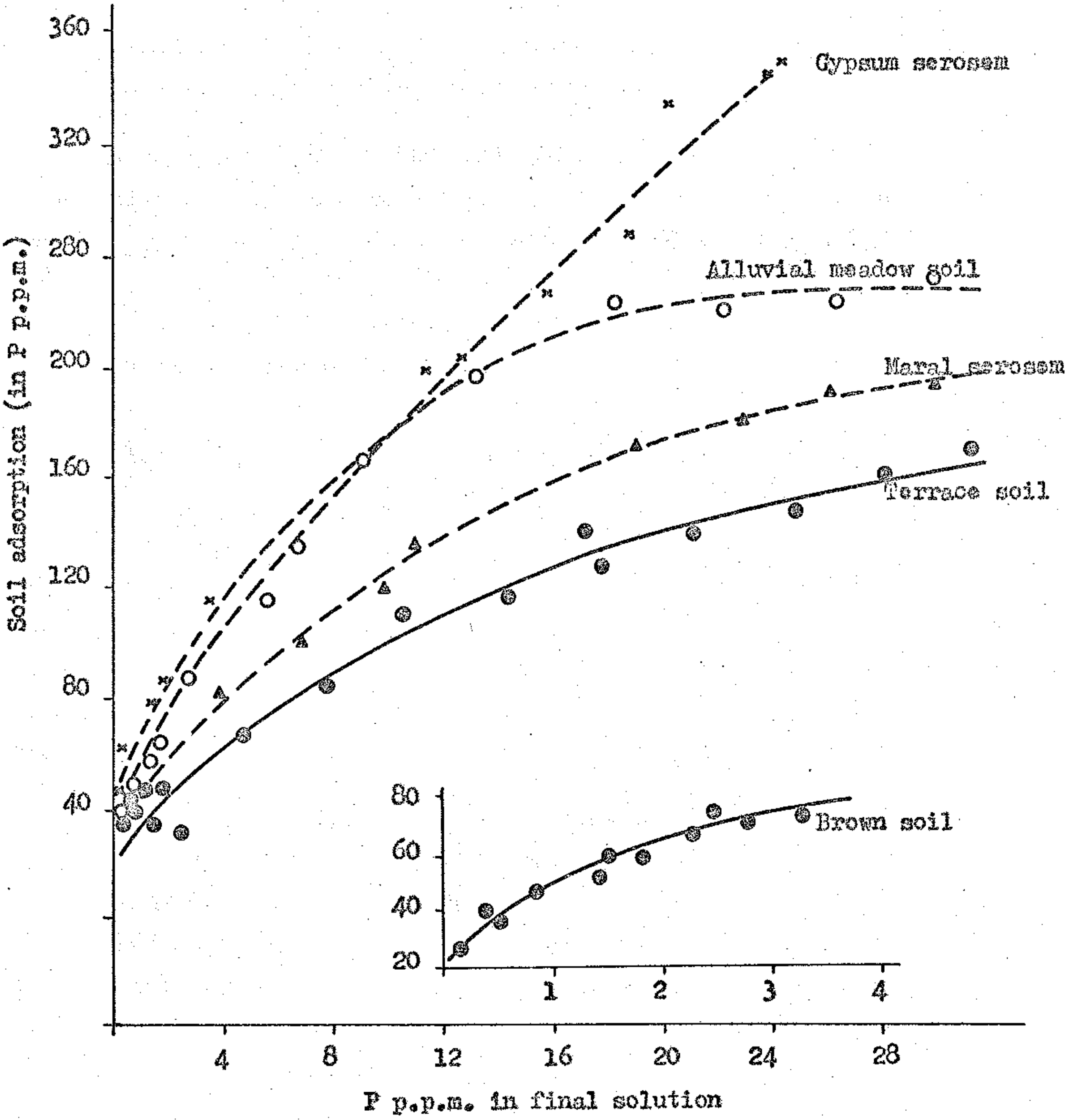
In graph 3, these values of the last column of table 21 were plotted in relation to the phosphorus concentration in final solution, both data being expressed in P. p.p.m.-

In this way, we can see and appreciate the phosphorus sorption -

Graph 3

P adsorption values related to P in final solution

(KH$_2$PO$_4$ method)



curve for these solis, but we cannot know up to which range of phosphorus concentration in final solution it has been produced bu the adsorption phenomena. In order to obtain this information, the data has been plotted as follows:

$$\frac{C \times 10^3}{X/m} \quad \text{in relation to C}$$

where

C = P concentration in final solution: it was expressed in (P p.p.m.)
X/m = amount of P sorbed by soil (P p.p.m.)

In graph 4 we can see that all these soils follow the Langmuir isotherm under a 20 p.p.m. P concentration in final solution and this agrees with that reported by Rennie et al 1959 (134), Olsen and Watanable 1957 (122).

However, these soils have shown the following features:

Soils	Breaks in the line of isotherm at P concentration in final solution.	
	1	2
Gypsum serosem	2.92	13.54
Marly serosem	1.75	17.20
Terrace soil	2.65	17.95
Alluvial meadow soil	1.65	9.34
Brown soil	1.46	---

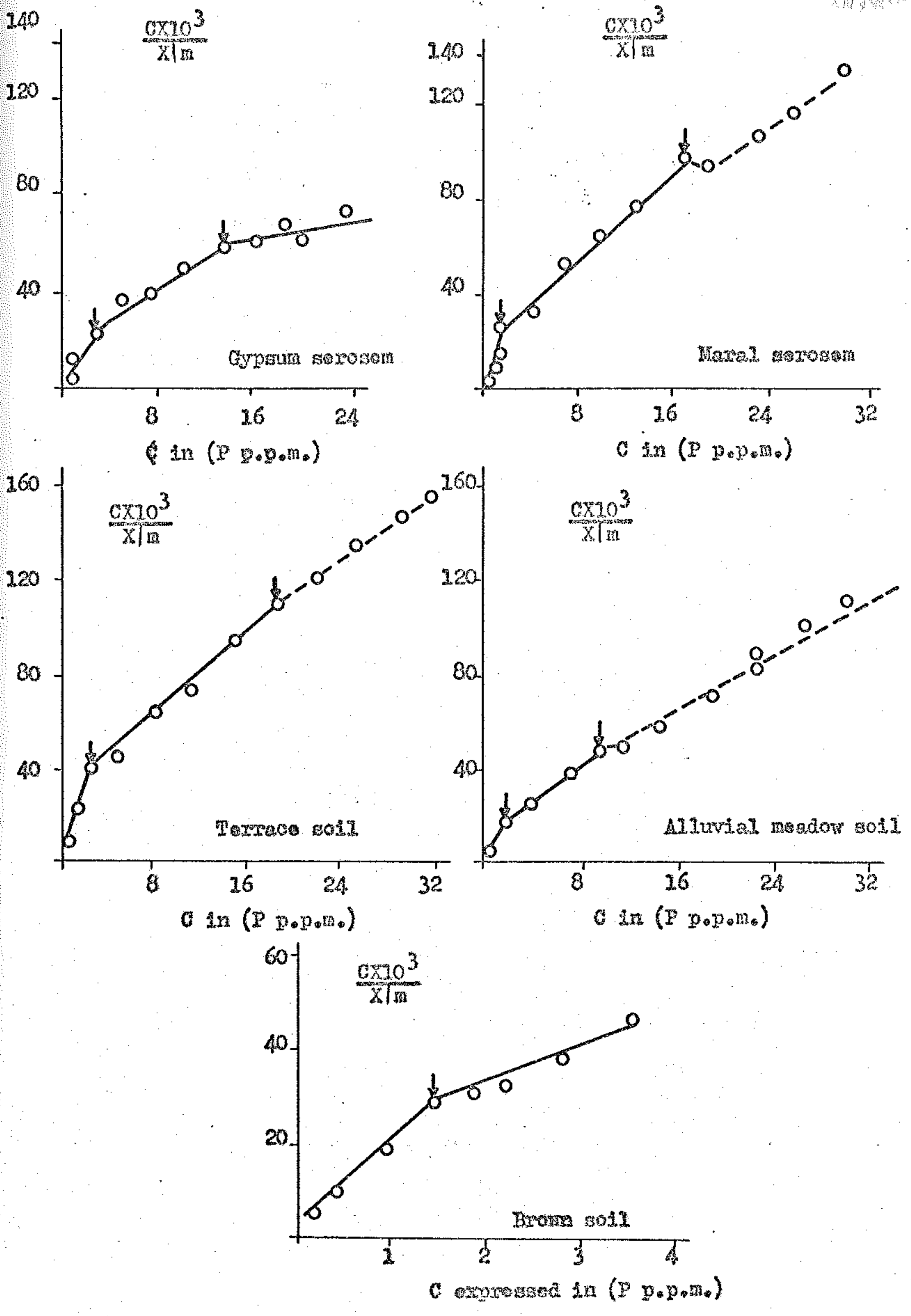
In these soils, the breaks in the line of the isotherm indicate the existence of two different sites for phosphorus adsorption complying with that reported by Syers et al 1973 (155); Muljadi et al 1966 (116,117), de Hoan 1966 (69), Harter R.D. 1969 (78), and we do not believe that it is due to a wrong determination or plotting as was stated by Gunary D.1970 (68).

If the conventional equation for the Langmuir isotherm is used

Graph 4

Plotting of $C \times 10^3/X|m$ values to C (Langmuir conventional equation)

Breaks in these line Isotherms are indicated by arrows



$$\frac{C}{X/m} = \frac{1}{K_1 \quad K_2} + \frac{C}{K_2} \qquad \text{(equation 1)}$$

where

C = P concentration in final solution

X/m = amount of P adsorbed by unit soil weight

K_1 = constant related to energy-bounding between P and soil

K_2 = maximum P adsorption

By a statistical procedure (correlation) of $\frac{C \times 10^3}{X/m}$ related to C, we can calculate the K_2 (maximum P adsorption) and the bounding energy (K_1) which will be equal to gradient^{-1} and gradient/intercept respectively.

In table 22 can be seen the regression equations, correlation coefficients and K_1, K_2 values for the Site I in these soils.

TABLE 22

Regression equations, correlation coefficients and K_1, K_2 values in the site I of P adsorption.

Soils	Regression equations		Values	
			K_1 (cc/mg)	K_2 p.p.m. P
Gypsum serosem	Y=7.40 x + 4.00	0.99	2.72	141.00
Marly serosem	Y=11.50 x + 0.41	0.99	27.00	86.90
Terrace soil	Y=14.16 x + 0.08	0.99	188.80	70.60
Aluvial meadow soil	Y= 8.10 x + 1.09	0.99	7.40	123.00
Brown soil	Y=17.79 x + 2.89	0.99	6.10	55.00

From this table, we can deduce the following features among these soils:

1) Two calcareous soils (alluvial meadow soil and gypsum serosem) tend to have a similar K_2 alchough the energy bounding (K_1) is higher in the alluvial soil than in a gypsum serosem.

2) The other two calcareous soils (marly serosem and terrace soil) showed similar K_2 values but they are lower than the preceding group.

3) Brown soil exhibition the lowest K_2 value and an energy bounding value similar to that of alluvial meadow soil from the River Gállego.

In order to have the K_1 and K_2 values in the site II, it is necessary to subtract the maximum P adsorption in site I from each of the X/m values in the range of P concentration in final solution related to site II and again calculate the regression equation between $^{C}/X/m$ and C. In this way, it was possible to have these K_1 and K_2 values, discarding the former $^{C}/X/m$ values because they were already out of the regression libe due to the fact that these C values are too low; avoiding errors in the calculation, such as was indicated by Syers et al 1973 (155).

TABLE 23

K_1 and K_2 values in the site II after the above mentioned correction of X/m values.

Soils	Regression equation	Values	
		K_1 cc/mg	K_2 P p.p.m.
Gypsum serosem	0.99 y=4.3x+ 78.3	0.05	220
Marly serosem	0.99 y=10.0x+20.9	0.47	99.7
Terrace soil	0.99 y=7.4x+69.0	0.12	135.2
Alluvial meadow soil	- It was not possible to correct		

In table 24 there were included the values calculated for the total maximum P adsorption in site II and in the last column of this table the K_2 values (sum of K_2 values from tables 22 and 23).

TABLE 24

K_1 and K_2 values in site II

Soils	r	Regression equation	Values		
			K_1	K_2	K_2
Gysum serosem	0.98	y=3.11 x + 15.63	0.19	322.0	361.0
Marly serosem	0.98	y=4.82 x + 14.31	0.33	207.4	187.0
Terrace soil	0.99	y=4.74 x + 24.8	0.19	211.1	205.8
Alluvial meadow soil	0.99	y=4.2 x + 8.39	0.50	238.0	——

From this table it can be appreciated that the estimation of total maximum P adsorption was suitable since similar K_2 values were obtained.

Several soil workens (Fried et al 1967) (57), de Hoan 1965 ( ), Syers et al 1973 (155) have used another expression of this isotherm which they have denominated modified equation of Langmuir, due to the fact that with this equation the adsorption sites are more accurately detected.

This modified Langmuir equation is:

$$X/m \text{ x } K_2^{\,I} - \frac{X/m}{K_1^{\,I}\ c} + K_2^{\,II} - \frac{X/m^{II}}{K_1^{\,II}\ c} \qquad \text{(equation 2)}$$

Meaning:

X/m = P adsorbed by soil
K_2 = maximum P adsorption
K_1 = a constant related to energy bounding between P and soil
C = P concentration in final solution.

The suffixes I and II refer to sites I and II for adsorption.

For a given site, the plotting of the X/m values against the $X/m/C$ valves gives a straight line in which K_2 is the intercept and K_1 gradient^{-1}.

In our case, the X/m values were expressed in mg P/100 g soil and C as P mol x 10^{-5} per litre.

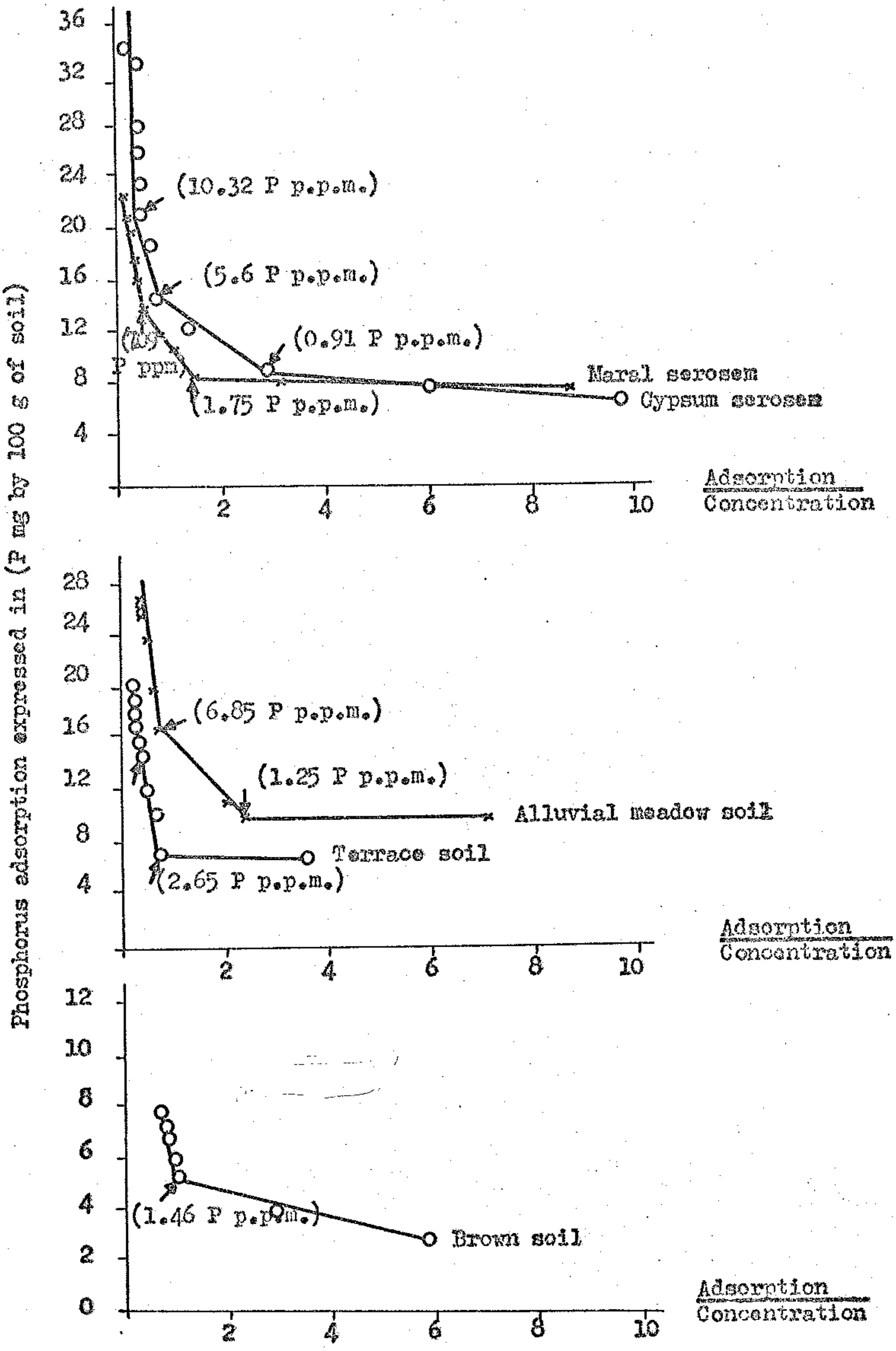
The plotting of these above values can be seen in graph 5.

Once again, the soils have shown the following breaks in the line which belong to the following P concentration in the final solution.

Graph 5

Plotting P adsorption data according to the arranged Langmuir Isotherm

Breaks in these lines are indicated by arrows



Soils	I	II	III
Gypsum serosem	0.91	5.6	10.32
Marly serosem	1.75	7.09	—
Terrace soil	2.65	7.95	—
Alluvial meadow soil from River Gállego	1.25	6.85	—
Brown soil	1.46	—	—

It was seen that, with equation 1 as with equation 2, it was possible the detection of the adsorption sites in these soils. However, equation 2 marks more precisely these sites of adsorption since it relects site I at lower P concentration (1-2 P p.p.m.) that is approximately of the same magnitude as those reported by de Hoan 1966 (69), Syers et al 1973 (155); while in site II it was defined at a lower P concentration than that found by equation 1.

Gypsum serosem showed another site for adsorption at 10.32 P p.p.m. concentration in final solution.

In table 25 the K_1 and K_2 values in sites I, II and III are included.

TABLE 25

K_1 and K_2 values in the different sites of adsorption. This data is expressed in (mg P/cc and mg P/100 g soil respectively).

Soils	Sites					
	I		II		III	
	K_1	K_2	K_1	K_2	K_1	K_2
Gypsum serosem	2.72	9.72	0.20	11.11	0.04	21.25
Marly serosem	6.60	8.85	0.16	8.86	—	—

(continuation of Table 25)

Terrace soil	18.18	7.03	0.07	12.90	—	—
Alluvial meadow soil	12.90	10.69	0.26	9.60	—	—
Brown soil	2.50	5.10	—	—	—	—

From this equation 2 it was observed that:

1) The four calcareous soils become similar in relation to the maximum P adsorption in site I, although there does not exist a direct ratio between this K_2 value and the energy constant (K_1 value).

2) Brown soil again showed the lowest K_2 value.

3) Calcareous soils exhibited a very weak energy (K_1) in site II.

4) The total maximum P adsorption from these soils was 25.50 and 70% for site II in the gypsum serosem, alluvial, marly serosem and terrace soils respectively.

In table 26 the K_2 values calculated by both equations have been summarized.

TABLE 26

K_2 values in sites I and II

Soils	Site I		Site II	
	Equation 1	Equation 2	Equation 1	Equation 2
Gypsum serosem	141.0	97.2	220.0	111.1
Marly serosem	86.0	88.5	99.7	88.6
Terrace soil	70.6	70.3	135.2	129.0

(continuation of Table 26)

Soils	Site I		Site II	
	Equation 1	Equation 2	Equation 1	Equation 2
Alluvial meadow soil	123.0	106.9	—	96.0
Brown soil	55.0	51.0	—	—

From this table it can be seen that for equation 1, in general the K_2 in I and II sites were slightly higher than those calculated by equation 2, agresing with that mentioned by Syers et al 1973 (155); except for terrace soil and marly serosem in site I where K_2 values by both equations were similar.

2. Method of calcium diphosphate in 0.01 M calcium chloride medium.

In table 27, the phosphorus sorption values according to this method are included. In this table can be seen the initial 0 concentration added, that obtained after 24 hour equilibrium and the P sorption by soil, calculated as the difference between both concentrations, divided by five due to the soil; solution ratio being (1:20) and, finally, the last column reflects these P sorption values + P surface.

TABLE 27

Phosphorus sorbed by soil expressed in (p.p.m. P) according to Ca $(H_2PO_4)2$, method.-

Soils	P concentration (g P/100 cc)			P sorbed by soil (in p.p.m. P)	
	Initial	Final	Difference	Difference/5	Difference/5 + surface P.
Gypsum serosem	100	16	84	16.8	41.8
	200	32	168	33.6	58.6
	300	50	250	50.0	75.0
	400	90	310	62.0	87.0
	800	200	600	120.0	145.0
	1600	720	880	176.0	201.0
	2000	996	1040	208.0	233.0
	2400	1040	1360	272.0	297.0
	2800	1400	1400	280.0	305.0
	3200	1800	1400	280.0	305.0
Marly serosem	100	36	64	12.8	52.8
	200	60	140	28.0	68.0
	300	92	208	41.6	81.6
	400	108	292	58.4	98.4
	800	380	420	84.0	124.0
	1600	920	680	136.0	176.0
	2000	1160	840	168.0	208.0
	2400	1500	900	180.0	220.0
	2800	1850	950	190.0	230.0
	3200	2200	1000	200.0	240.0
Terrace soil	100	36	64	12.8	55.8
	200	52	148	29.6	72.6
	300	78	222	44.4	87.4
	400	108	292	58.4	104.4
	800	400	400	80.0	123.0
	1600	1100	500	110.0	153.0
	2000	1400	600	120.0	163.0
	2400	1650	650	130.0	173.0
	2800	2100	700	140.0	183.0
	3200	2450	750	150.0	193.0

(continuation of Table 27)

Phosphorus sorbed by soil expressed in (p.p.m. P) according to Ca $(H_2 PO_4)2$. method.

Soils	P concentration (g P/100 cc)			P sorbed by soil (in p.p.m. P)	
	Initial	Final	Difference	Difference/5	Difference/5 + surface P.
Alluvial meadow soil from River Gállego	100	25	75	15.0	85.0
	200	60	140	28.0	98.0
	300	104	196	39.6	109.6
	400	110	290	54.0	124.0
	800	380	420	85.0	155.0
	1000	900	700	140.0	210.0
	2000	1200	800	160.0	230.0
	2400	1550	850	170.0	240.0
	2800	1900	900	180.0	250.0
	3200	2200	1000	200.0	270.0
Brown soil	100	22	78	15.6	31.6
	200	50	120	24.0	40.0
	300	150	150	30.0	46.0
	400	230	170	34.0	50.0
	800	540	260	52.0	68.0
	1200	800	400	80.0	96.0
	1600	1160	440	88.0	104.0

These values of the last column in table 27, were plotted in relation to C in final solution. Both values being expressed in P p.p.m. (graph 6).

In this way, we can observe how the curves of phosphorus sorption by these soils are, however we ignore up to which P concentration, adsorption by soil takes place. Thus, if we plot in graph 7, the $C \times 10^3/X/m$ values related to C, we can see that all these soils follow the Langmuir isotherm under 20 p.p.m. P concentration in final solution. For the above soils the Langmuir isotherm holds, until the following P concentration.

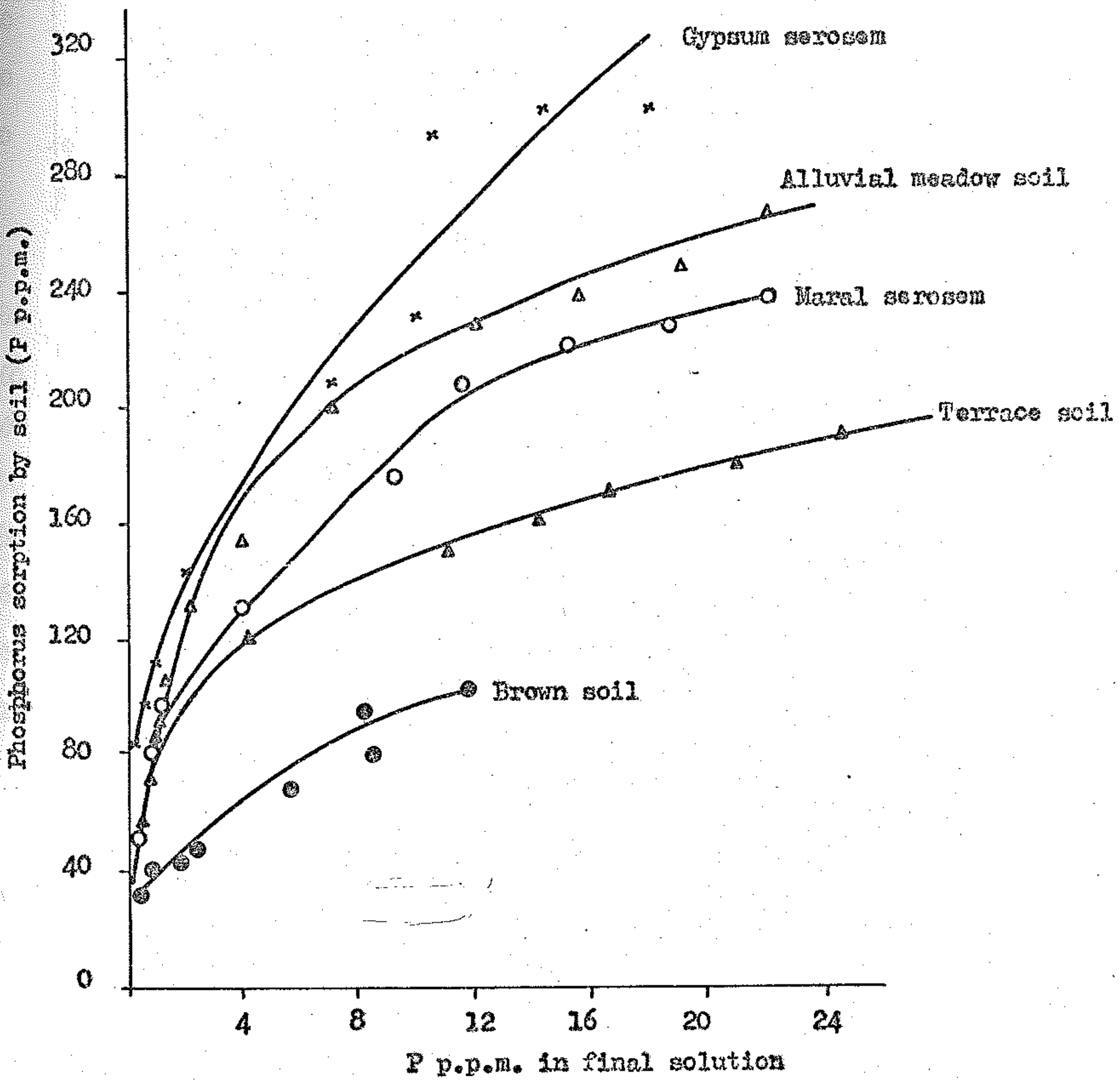
Soils	P p.p.m. in final solution
Gypsum serosem	7.20
Marly serosem	3.80
Terrace soil	11.00
Alluvial meadow soil	9.00
Brown soil	2.30

According to this laboratory procedure, these soils follow the Langmuir isotherm at a lower range of P concentration than that obtained with the former method (potassium diphosphate solutions buffered at pH 7). In fact, the P adsorption values were slightly higher than those found by the former method, agreeing with that published by Rajan S.S. and Fox R.L. 1972 (132) in a study concerned with adsorption with different P salts, equilibrium time and salts added.

By using the conventional Langmuir equation (equation 1), the K_1 and K_2 values were calculated and included in table 28.

Graph 6

P sorption values related to P in final solution. [$(Ca)_2 (H_2PO_4)$ in 0.01 M Ca_2Cl method]



Graph 7

P adsorption values according to the conventional Lang-muir Isotherms. Breaks in these line are indicated by anows

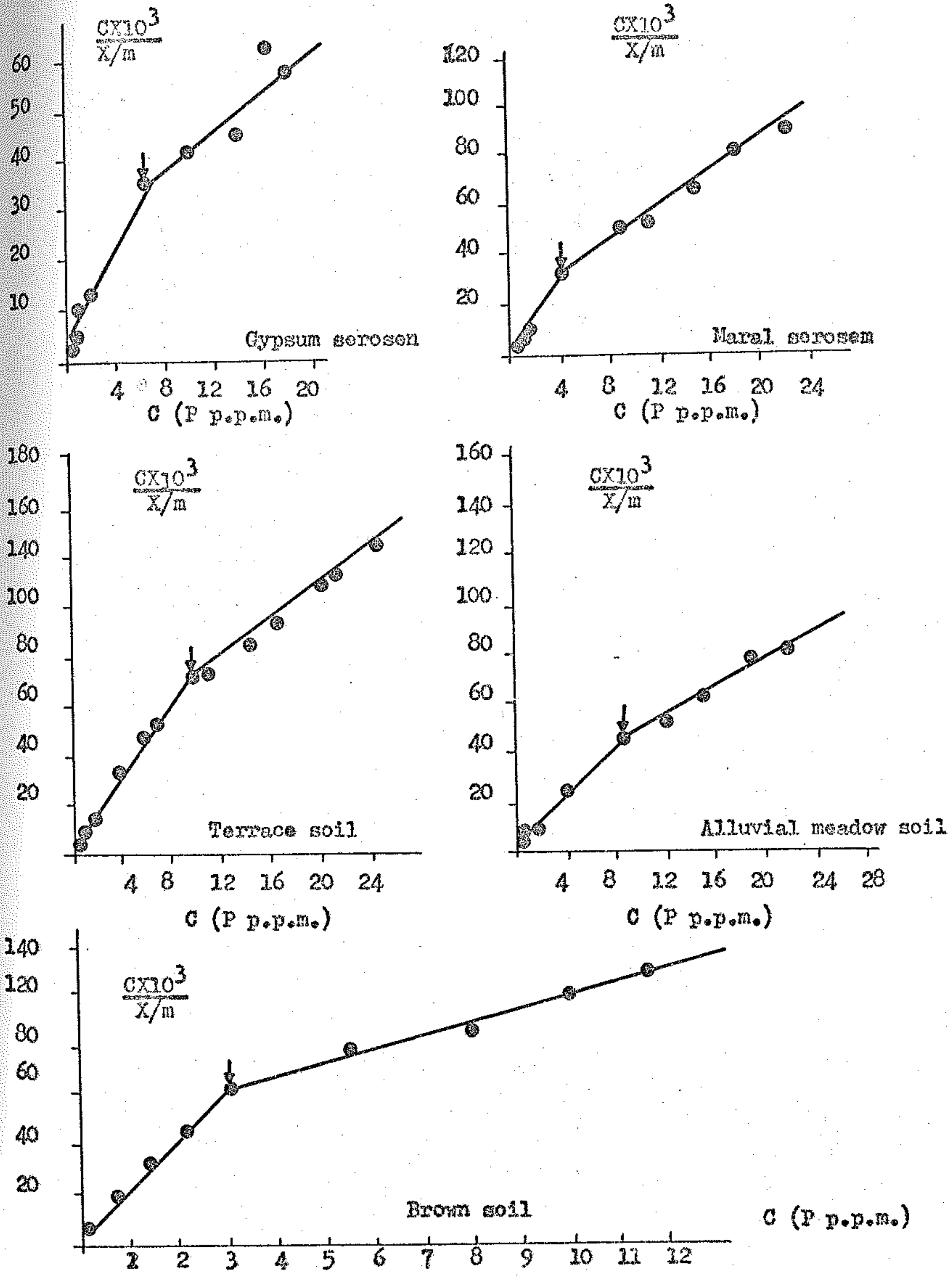


TABLE 28

Regression equations, correlation coefficients (r) and K_1, K_2 data

Soils	r	Regression equation	Values	
			K_1 cc/mg	K_2 (ppm P)
Gypsum serosem	0.98	$y=4.38\ x + 4.55$	0.96	230
Marly serosem	0.99	$y=6.89\ x + 4.39$	1.57	150
Terrace soil	0.99	$y=6.22\ x + 4.50$	1.38	160
Alluvial meadow soil	0.99	$y=4.48\ x + 4.01$	1.12	220
Brown soil	0.99	$y=18.61\ x + 3.97$	4.69	50

According to this table, we deduce that:

There exist differences among these soils related to K_1 and K_2 values.

Brown soil has shown the highest value of K_1 (energy bounding -P-soil) and the lowest value of K_2. In the four calcareous soils an inverse ratio between K_1 and K_2 can be observed, disagreeing with the results reported by Syers et al 1971 (154) for the Brazilian tropical soils.

Formerly, the modified Langmuir equation (equation 2) was more precise in detecting the adsorption sites. For that reason, we make use of it once again in this method in order to see whether, with this laboratory method, the same fact is produced. So in graph 8 X/m values have been plotted against $^X/m/C$ values and the presence of two sites for P adsorption, in three calcareous soils and brown soils, was verified, due to the breaks in the line.

These breaks have taken place at the following P concentration in final solution.

Soils	I Site	II Site
Gypsum serosem	0.90 P ppm	7.20 P ppm
Marly serosem	3.80 "	—
Terrace soil	4.00 "	17.20 "
Alluvial meadow soil	1.04	3.80 "
Brown soil	0.80	2.30

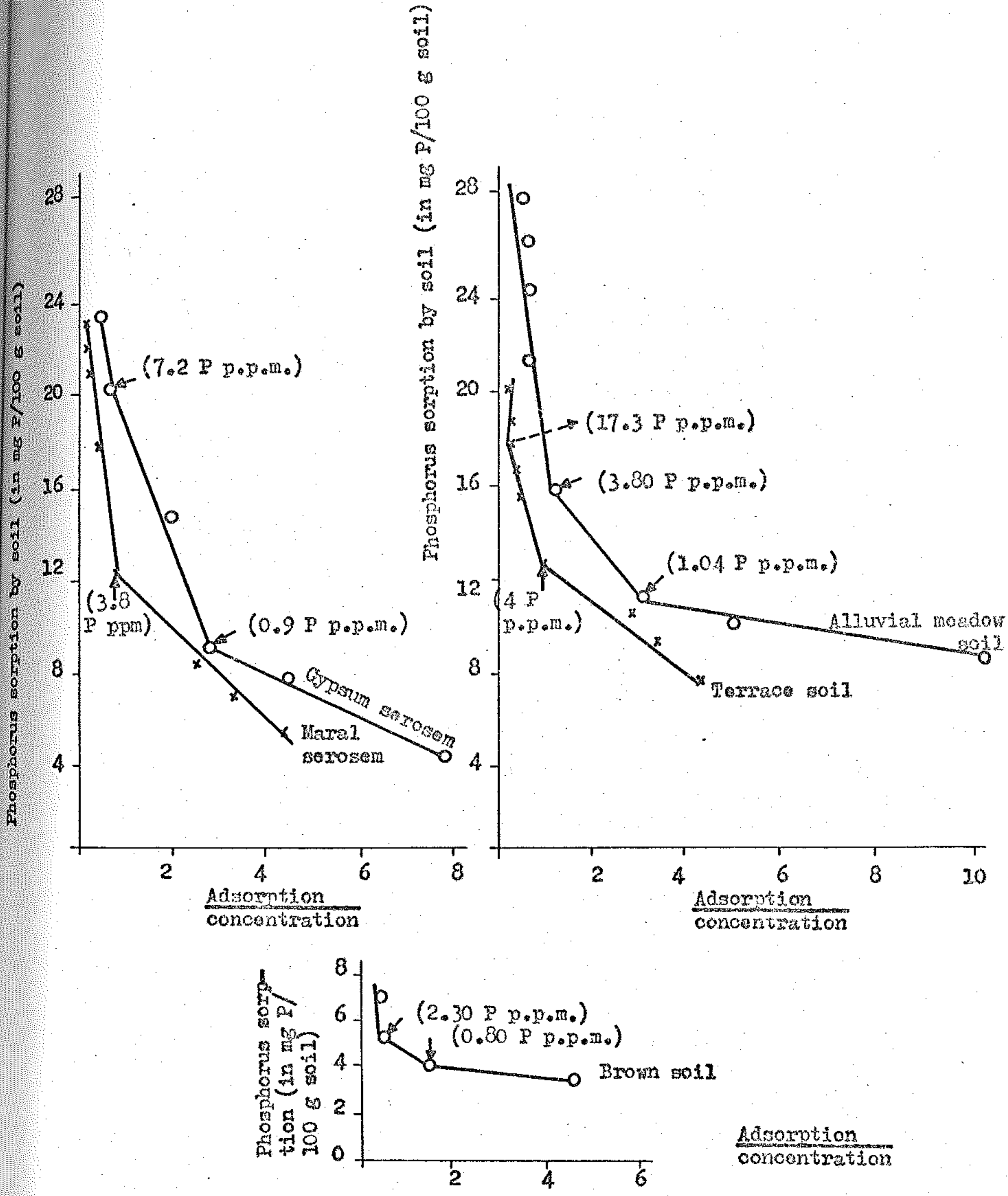
In this case, it is clear that equation 2 is more precise than equation 1 for detecting adsorption sites at lower P concentrations.

Two soils (marly serosem and terrace soil) have shown this I site at a slightly higher P concentration to that cited by Syers et al 1973 (155).

Graph 8

P adsorption values according to the arranged Langmuir Isotherm

Breaks in these lines are indicated by arrows



In table 29 the K_1 and K_2 values calculated according to equation 2 are included.

TABLE 29

K_1 and K_2 data in Sites I and II

Soils	Site I		Site II	
	K_1 (cc/mg)	K_2 (mg P/100g s.)	K_1 (cc/mg)	K_2 (mg P/100g. s.)
Gysum serosem	1.20	11.44	0.18	17.01
Marly serosem	0.53	14.30	—	—
Terrace soil	0.59	14.30	0.06	4.69
Alluvial meadow soil	3.12	11.70	0.44	6.70
Brown soil	3.45	4.40	0.89	1.31

From this data we can deduce that:

1) Brown soil again showed a K_1 value in site I and, as well, in site II higher than that of calcareous soils. Both adsorption sites have lower K_2 data than that corresponding to calcareous soils.

2) Calcareous soils in site I reflect the same ratio for K_1 and K_2 values found by equation 1, believing that the marly serosem and terrace soils supply the P adsorbed more easily than the others.

3) In all soils, the K_1 value in site I is 8-16 times higher than those in site II.

4) In all soils, except marly serosem, the P adsorption was higher in site I than in II, being approximately 75,74,64 and 44% of the total maximum P adsorption for the brown, terrace, alluvial meadow and gypsum serosem soil respectively.

3. Comparison between both laboratory methods.

In this part, we shall try to compare both methods in order to select one of them for later studies.

In table 30 we have summarized the K_2 values obtained by both methods (data from tables 25 and 29).

TABLE 30

K_2 values in Sites I and II obtained by both laboratory procedures. Data is expressed (in mg P/100 g soil).

Soils	Site I		Site II		Site III
	KH_2PO_4	$Ca(H_2PO_4)_2$	KH_2PO_4	$Ca(H_2PO_4)_2$	KH_2PO_4
Gypsum serosem	9.72	11.44	11.11	14.01	21.25
Marly serosem	8.85	14.30	8.86	—	—
Terrace soil	7.03	14.30	12.90	4.69	—
Alluvial meadow soil	10.69	11.70	9.60	6.70	—
Brown soil	5.10	4.40	—	1.31	—

From this data we deduce that:

1) Both procedures reflect the same tendency in the pattern of P adsorption by these soils, that is that gypsum serosem has the highest total maximum P adsorption, while brown soil was the soil that has adsorbed less P, the other three (marly serosem, terrace soil and alluvial meadow soil) being included between both values.

2) In site I, K_2 values got by both methods were similar for three soils (gypsum serosem, alluvial meadow soil and brown soil); however, for the other two soils (terrace soil and marly serosem) they are completely different; that can be explained because in the first procedure these soils followed the Langmuir isotherm at a lower P concentration than in the second method. Reflecting, in the case of marly serosem, the presence of a single site for P adsorption situated at low P concentration, while for terrace soil the P adsorption predominates in site I, being of lower quantity in site II.

If we select the calcium diphosphate in 0.0.1 calcium chloride medium, we believe quite sincerely that we shall not be wrong in the estimation of total maximum P adsorption for the following reasons:

1) By both procedures, brown soil shows the same value of total K_2, with the advantage that the latter method has reflected two adsorption sites (I and II).

2) For calcareous soils, 0.01 M calcium chloride medium can better simulate the calcium concentration in these soils.

3) The fact that Cole and Olsen 1959 (38) used, in a posterior study a 0.01 M Medium of Cl_2Ca and calcium diphosphate in studies concerned with the estimation of P adsorption in calcareous soils is a positive point to take into account.

As has been seen in these pages, we found differences among these soils (calcareous and brown soils) related to P adsorption. Well, we can justify this different data of P adsorption due to the fact these soils have different clay contents, there existing a significant ratio (r = 0.95 and 0.99) between this clay content and total maximum P adsorption calculated by both laboratory procedures.

In calcareous soils, there was no significant correlation between total maximum P adsorption and % calcium carbonate; it may be that this soil constituent influences simultaneously with clay on this adsorption.

4. Buffering Capacity Factor

Recently, several soil workers believe that the buffering capacity factor must be taken into account for suitable evaluations of P needs in a soil and thus to be able to fix the requirements of P fertilizers for a soil.

This factor has been defined as the P adsorbed amount at a certain P concentration in final solution.

Ozanne et al 1968 (124), Barrow 1967 (13), Rajan S.S. 1973 (133) have used calcium diphosphate in 0.01 M calcium chloride medium, because they consider that this is similar to that which is found in the soils under normal conditions.

This buffering capacity factor has been calculated at different ranges of P concentration in final solution.

Ozanne et al 1968 (124) have considered a range from 0.25 to 0.35 P p.p.m., since these authors found maximum crop yields at 0.30 p.p.m. Barrow 1967 (13) believes that 0.20 P p.p.m. is a suitable concentration and Pardo Fernandez Mª T. 1972 (125) mentioned that it is allowed at any P range in which the Langmuir isotherm is followed.

Although in this study phosphorus dressings were not applied, we believe that it will be useful to have information about these soils concerning this factor.

In order to calculate it, we have used a range of 0.50 to 0.60 P p.p.m. concentration, based on the criterion of Ozanne et al 1968 (124) who have worked with soils that show similar features to ours and these authors have studied this factor in a soil: solution ratio 1:10 whilst ours has been a 1:20 ratio. The accuracy of this range chosen must be checked in the future with phosphorus fertilizer trials.

In graph 9, the P adsorption values related to the 0 - 1 p.p.m. P range in final solution have been plotted. From this graph, we have calculated this buffering capacity factor as the P adsorbed amount between 0.5. to 0.6 P p.p.m.

This buffering capacity factor in these soils is:

Soils	Buffering capacity factor expressed in p.p.m. P.	Site I values K_1	Site I values K_2
Gypsum serosem	3.10	114.4	1.20
Marly serosem	6.00	143.0	0.53
Terrace soil	4.63	143.0	0.59
Alluvial meadow soil	2.89	117.0	3.12
Brown soil	2.00	44.0	3.45

There exists a significant ratio ($r = 0.90$) between this factor and the K_2 value in site I, being of the same magnitude as that found by Rajan S.S. 1973 (133), it being possible, therefore, to say that at this P concentration a suitable supply of this nutrient to plants will occur.

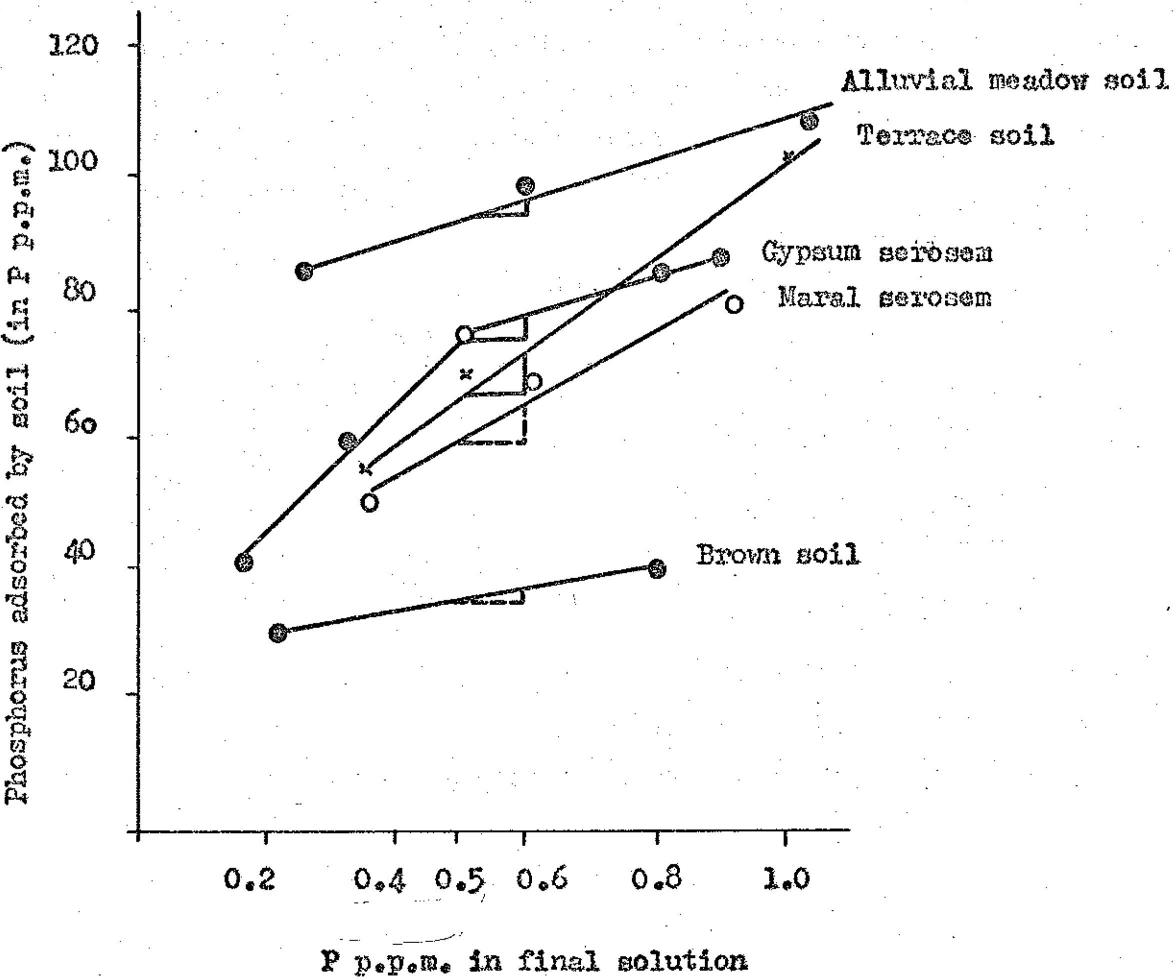
In general, it agrees with that reported by Syers et al 1971 (153) in which the soils with high P adsorption exhibit a lesser P desorption, except for terrace soil in which this P liberated was similar to that shown by brown soil.

This terrace soil has a similar P adsorption as marly serosem, but the latter showed a lower % P desorbed. This fact can be explained as in terrace soil there exists a predominance of the area I of P desorption over the area II related to chemio desorption. In fact, these P liberated were 58% of the total amount desorbed.

It seems that in the transfer of P adsorbed there influences the amount adsorbed, energy bounding P-soil and, finally, the mechanism by which the P adsorption by the soil can be produced.

Graph 9

P adsorbed by soil related to P in final solution



B. PHOSPHORUS DESORPTION

In chapter 1, outlining the purpose of this study, it was pointed out that the finality of this part is to get information concerning the desorption of P from the soild phase to soil solution. For that purpose, two laboratory procedures were used, one of them consisting of 14 water extraction on the same soil sample (method of Fried et al 1956 (55), the other being the one prescribed by Amer et al 1955 (4) in which a system formed by water-anion-resin-soil is used at different equilibrium times.

Due to the nature of both procedures, we can evaluate how this desorption occurs. The former will furnish us with a general idea of this process and the latter will reflect the different reactions that take place in the desorption according to time. The latter would also have been appreciated if we had used another of the procedures proposed by Fried et al 1956 (55); however, we believed that the Amer method would be more precise because the continuous water leaching method furnishes low P values and there exist problems concerned with the first water leaching due to turbidity. On the contrary, the resin method, in spite of its use in the laboratory being longer and more tedious, facilitates the colour metric P determination since it supplies higher values in this nutrient.

1. Method of 14 water extractions on the same soil sample

In the presence of water, it is believed that the phosphorus transfer from solid phase to soil solution is due to a hydrolitic displacement reaction and it can be represented by the following equation:

$$\text{P soil} \quad \underset{K_2 \text{ x soil-OH}}{\overset{K_1 \text{ x OH}}{\rightleftarrows}} \quad \text{P in soil solution}$$

In which P-soil is in equilibrium with P in solution, so as the P of this liquid phase is evaluated, it will furnish us with an estimation of which it is easily transferible from the solid phase. In each of the 14 water extractions we have had the above equilibrium and the P obtained in each water extraction has been analysed. (please see table 31).

This data from table 31 has been plotted in relation to the number of extractions in graph 10.

For the shape of these desorption curves, gypsum serosem, marly serosem and brown soil, their phosphorus transfer was controlled by the solubility of their P compounds, while in the other calcareous soils (terrace soil and alluvial meadow soil) it can be interpreted as a typical desorption.

In this laboratory method, equilibrium time for each extraction was 1 hour and a quantity of P desorbed was obtained. Therefore, if we plotted this data of P desorbed according to equilibrium time, we find that there exists a close correlation ($r = 0.99 - 0.96$) for all soils. From this it is deduced that Fick's law, proposed by Larsen and Cooke I.J. 1970 (102) for the P transfer from solid phase to soil solution is applicable.

$$y = R + b\,t.$$

where

y = amount of P desorbed
R = initial P quantity in soil solution
b = rate of P desorption
t = time

Graph 10

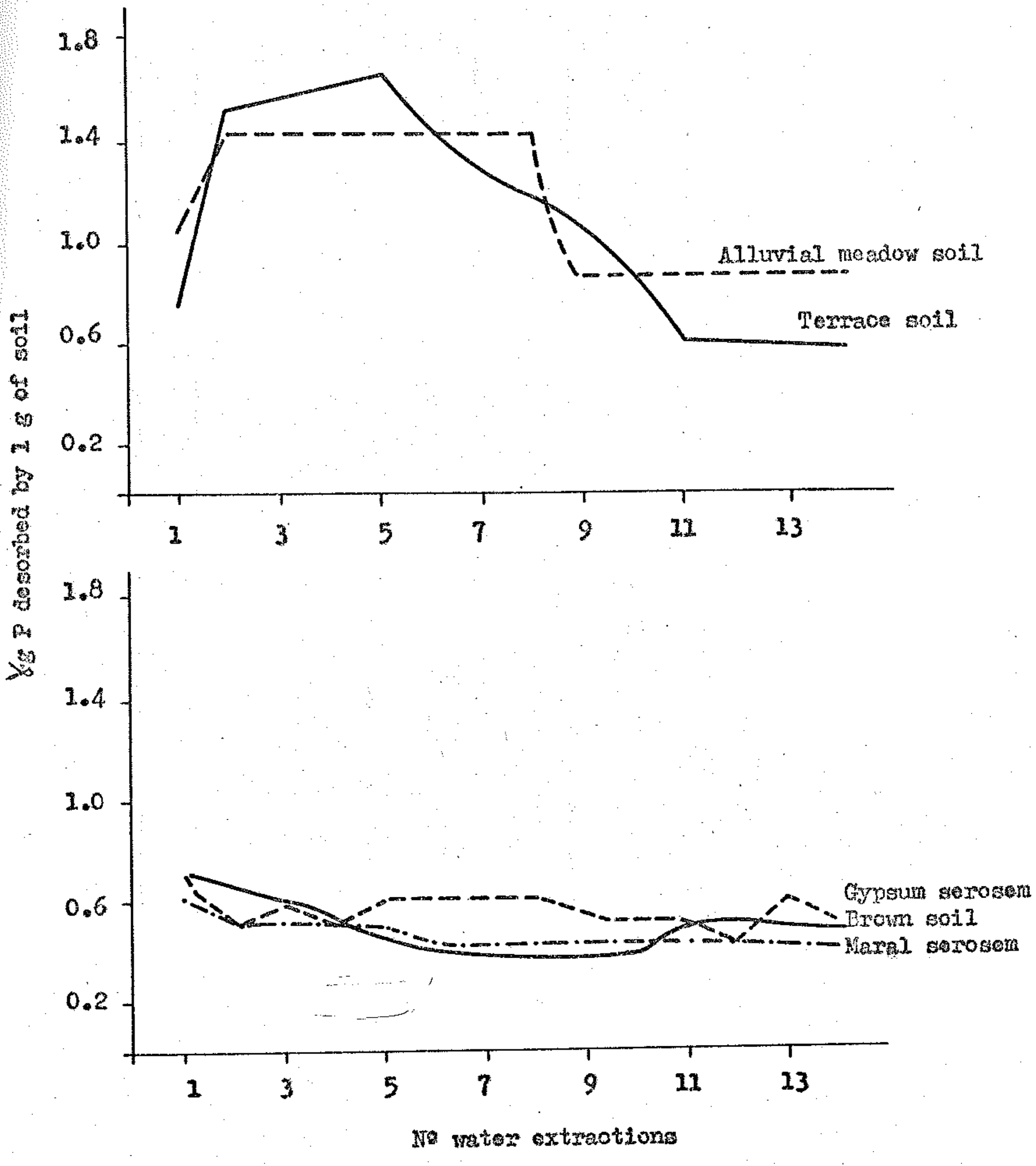

1.8
1.4
1.0
0.6
0.2
1
3
5
7
9
11
13
Alluvial meadow soil
Terrace soil
γg P desorbed by 1 g of soil
1.8
1.4
1.0
0.6
0.2
1
3
5
7
9
11
13
Gypsum serosem
Brown soil
Maral serosem
Nº water extractions

TABLE 31

P desorbed according to the 14 water extractions (values are expressed in P. p.p.m.)

Soils	Number of soil extraction														
Gypsum serosem	0.616	0.538	8.580	0.528	0.616	0.616	0.616	0.616	0.520	0.520	0.528	0.440	0.616	0.528	7.874
Marly serosem	0.700	0.530	0.530	0.528	0.528	0.440	0.440	0.440	0.440	0.440	0.440	0.440	0.440	0.440	6.770
Terrace soil	0.768	1.520	1.520	1.520	1.650	1.460	1.270	1.200	1.080	0.980	0.600	0.600	0.600	0.600	15.300
Alluvial meadow soil	1.040	1.440	1.440	1.440	1.440	1.460	1.440	0.860	0.860	0.860	0.860	0.860	0.860	0.860	16.300
Brown soil	0.730	0.650	0.600	0.520	0.470	0.430	0.430	0.430	0.430	0.430	0.490	0.490	0.490	0.490	7.080

These R and L values ware in these soils as follows:

Soils	R	b
Gypsum serosem	0.17	0.55
Marly serosem	0.47	0.46
Terrace soil	0.80	1.14
Alluvial meadow soil from River Gállego	0.64	1.19
Brown soil	0.49	0.47

Suggesting that:

1) Alluvial meadow soil and terrace soil have similar rates of P desorption although the latter showed a slightly higher R value.

2) Marly serosem and brown soile behave similarly.

3) Gypsum serosem had an intermediate pattern batween the preceding two groups.

2. Water-Anionic resin-soil system.

In this case, the above mentioned equilibrium has taken place also and thers only exists the difference that the P desorbed from the soil is adsorbed by an anionic rasin introduced in the water soil suspension.

In table 32 these values can be seen. The proceding P values have been compared in relation to time in graph 11. For the shape of these phosphorus desorption curves only a moderate reaction of P transfer has occured. Therefore, marly serosem starts with a 4.84 P ppm value until it reaches a constant value of 21.50 P ppm at 24 hours, while gypsum holds a similar value until 4 hours and from this time the moderate reaction takes place, reaching a constant 37.60 P ppm at 24 hours.

In the other calcareous soils (terrace soil and alluvial meadow soil) the process starts with 16.12 and 30.10 P ppm respectively, reaching later a constant value of 51.6 and 54.8 P ppm in 24 hours.

Brown soil showed the lowest initial value 2.2 P ppm and at 48 hours, a value of 24 P ppm was reached.

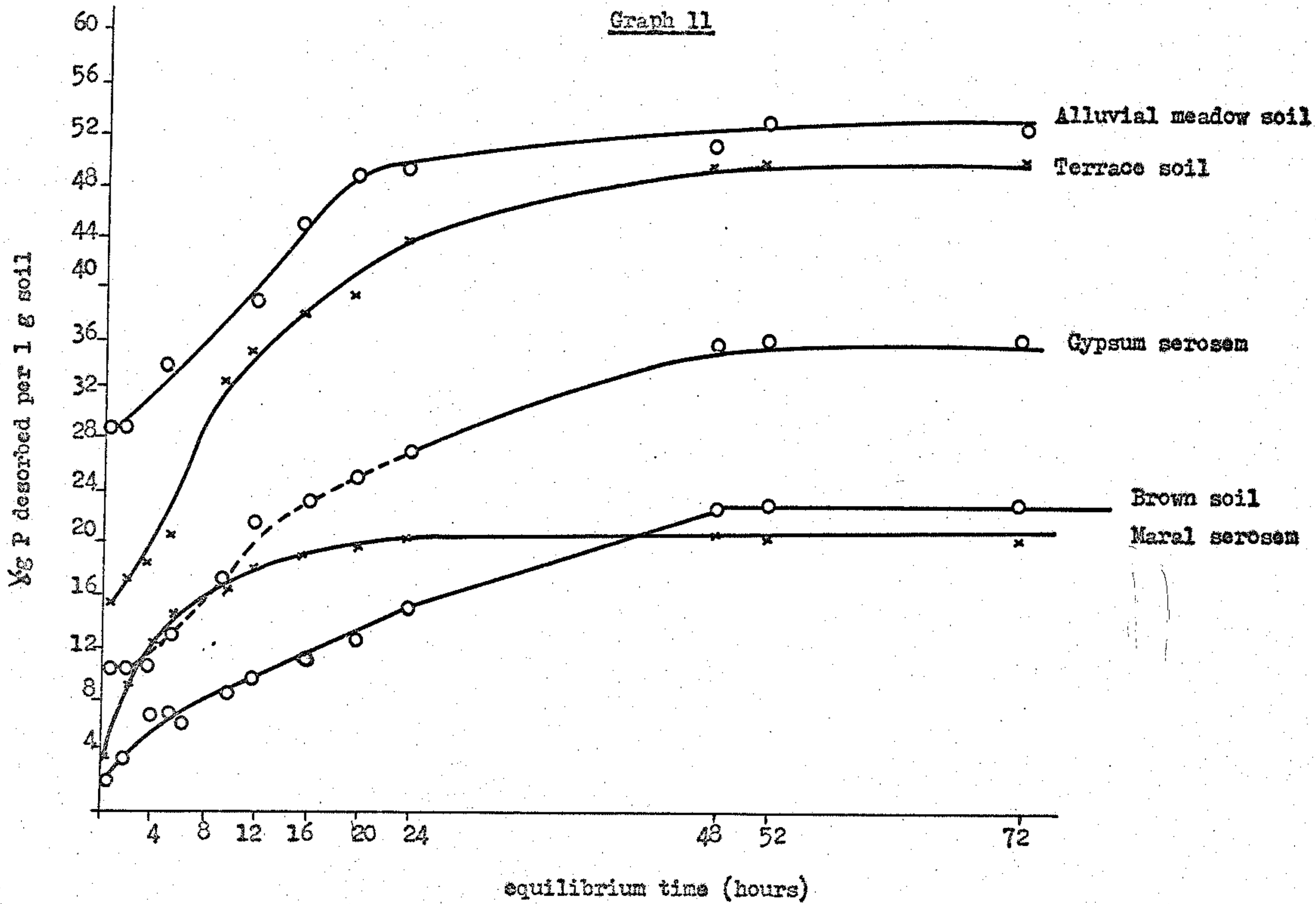
It was mentioned before that the presence of a single moderate reaction of P transfer was due to finding, at times lower than 1 hour, this same P value. For that reason we believe that this P value can be considered as the P already present in the soil solution. That can agree with that published by Thompson el al 1960 (158) in some soils studied by them.

In order to see how the kinetics of this process was, let us consider the criterion of Amer el al 1955 (4) who pointed out that the amount of P adsorbed by an anionic resin et a t time will be equeal to:

$$Pr = Pr_1 + Pr_2 + Pr_3$$

Pr_1, Pr_2 and Pr_3 being the P adsorbed by the resin as a consequence of the quick, moderate and slow reactions which have taken place in a soil.

Graph 11


60
56
52
48
44
40
36
32
28
24
20
16
12
8
4
γg P desorbed per 1 g soil
4
8
12
16
20
24
48
52
72
equilibrium time (hours)
Alluvial meadow soil
Terrace soil
Gypsum serosem
Brown soil
Maral serosem

Since the rate of P adsorption by resin in each reaction will be proportional to the amount of P not adsorbed which remains in the soil solid phase, the following equation will be written

$$d\ Pr_1/dt = K_1'\ P_{51}$$

$$d\ Pr_2/dt = K_2'\ P_{52}$$

$$d\ Pr_3/dt = K_3'\ P_{53}$$

in which:

P_{51}, P_{52} and P_{53} represent the amounts of P not adsorbed and they will be contributed to the respective reactions at t time. K_1, K_2 and K_3 are constant.

The above equation will be integrated and they will have the form:

$$Pr_1 = C_1\ (1-e^{-K_1\ t})$$
$$Pr_2 = C_2\ (1-e-^{K_2\ t})$$
$$Pr_3 = C_3\ (1-\ e-\ K_3\ t)$$

If the base e is changed to 10, C_1 will represent the initial amount of P_{51} in soil.

The total equation of this process will be:

$$Pr = Pr_1 + Pr_2 + Pr_3$$
$$Pr = (C_1+C_2+C_3\ ) - (C_1 x 10^{-K_1 t} + C_2 x 10^{-K_2 t} + C_3 x 10^{-K_3 t}\ )$$

Transfering $(C_1 + C_2 + C_3)$ to the other member of this equation one will have:

$$(C_1+C_2+C_3) - Pr = C_1 x 10^{-K_1 t} + C_2 x 10^{-K_2 t} + C_3 x 10^{-K_3 t}\ )$$

If we take logarithms at both members of this equation, we shall have its lineal expression:

$$Log\ (C_1+C_2+C_3\ - Pr) = log(C_1 x 10^{-K1t} + C_2 x 10^{-K_2 r} + C_3 x 10^{-K_3 t}\ )$$

In these soils only the moderate reaction takes place, which confirms that found by Thompson et al 1960 (158), Moser et al 1959 (115) in some soils.

Thus, the equation for these soils will be:

$$Log\ (C_1 + C_2\ - Pr) = log\ C_1 - K_1\ t + log\ C_2 - K_2\ t$$

At a longer equilibrium time, if the first reaction exists, this will have been reached and then C_1 x $10^{-K_1 t}$ will be insignificant and can be omitted.

Thus log $(C_1 + C_2 - Pr)$ will be drawn against time and then, the log C_2 and K_2 will be obteined, since they correspond to the intercept and gradient respectively.

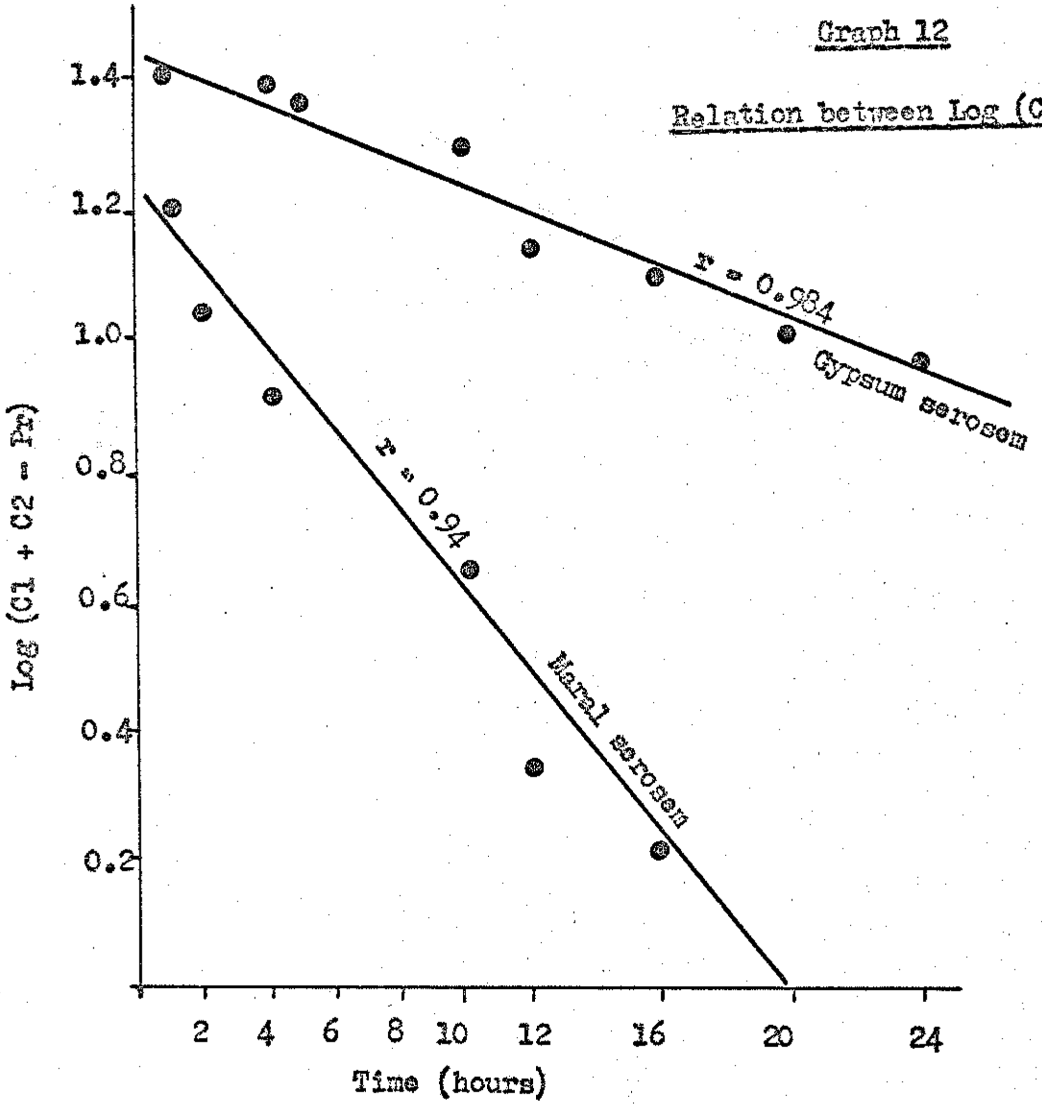
In these soils, $(C_1 + C_2)$ value was chosen as that obtained at 24 hours and Pr value was that obtained at each equilibrium time. In graphs 12 and 13 can be seen the drawing of these values. There was a close ratio between log $(C_1 + C_2 - Pr)$ and time that means a suitable choice of the $(C_1 + C_2)$ value in these soils.

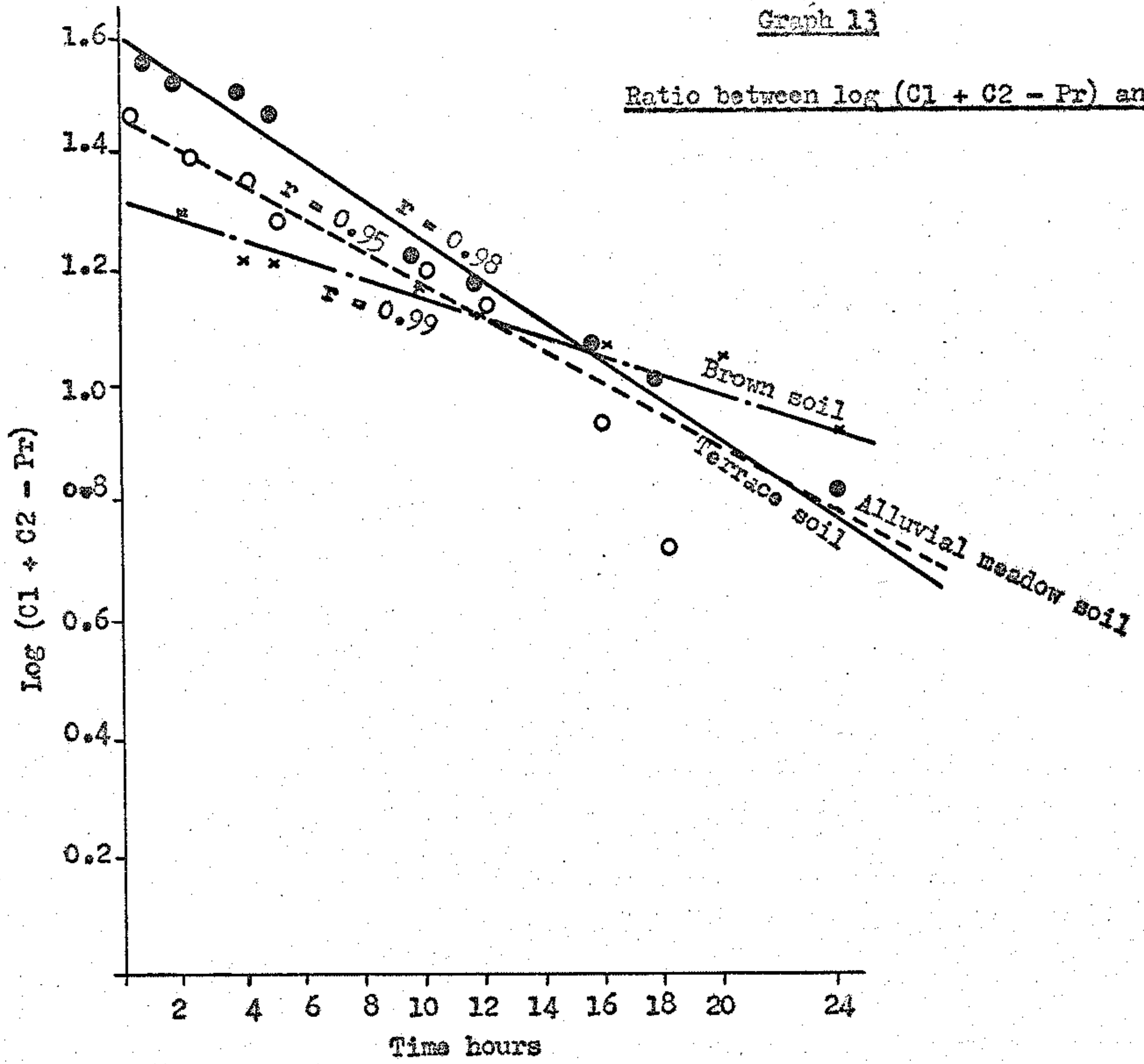
The equations for these soils were as follows:

Soils	
Gypsum serosem	$Pr = 37,6-(29,6x10^{-0.022t})$
Marly serosem	$Pr = 21.5-(15.1x10^{-0.061t})$
Terrace soil	$Pr = 51.6-(39.7x10^{-0.032t})$
Alluvial meadow soil	$Pr = 54.8-(28.7x10^{-0.033t})$
Brown soil	$Pr = 24.0-(21x10^{-0.015t})$

Graph 12

Relation between Log (C1 + C2 - Pr) and time





Graph 13

Ratio between log (C1 + C2 - Pr) and time

TABLE 32 : P adsorbed by anion resin, expressed in (P ppm).

Soils	Equilibrium time in hours											
	1	2	4	5	10	12	16	20	24	48	56	72
Gypsum serosem	11.20	11.80	11.80	13.90	17.20	23.65	24.75	26.88	28.48	37.60	37.60	37.60
Marly serosem	4.84	10.22	13.44	15.00	17.20	19.35	19.89	20.43	21.50	21.50	21.50	21.50
Terrace soil	16.12	18.28	19.35	22.58	34.40	36.55	39.78	40.85	45.75	51.60	51.60	51.60
Alluvial meadow soil	30.10	30.10	32.10	35.55	38.70	40.80	46.20	50.50	50.50	52.60	54.80	54.80
Brown soil	2.20	4.40	7.90	7.90	9.30	11.00	12.00	12.90	16.00	24.00	24.00	24.00

In table 33 can be seen the calculated P adsorbed values according to the above equations.

On the other hand, the anionic resin method gives, in general, results that agree with the scheme proposed by O. Talibudean 1957 (156). That means that in these soils the P desorbed has come from P quimiosorbed fixed on the internal surfaces of soil aggregates and micropores.

TABLE Nº 33 : Values of P adsorbed by anion resin, calculated according to the previous equations (expressed in P ppm).

Soils	Equilibrium time in hours											
	1	2	4	5	10	12	16	20	27	48	52	72
Gypsum serosem	9.54	10.93	13.50	17.69	19.81	21.50	24.50	26.80	28.90	35.20	35.50	38.90
Marly serosem	8.30	10.10	12.90	14.00	17.70	80.60	19.90	20.41	24.00	24.00	24.00	24.00
Terrace soil	15.00	18.00	22.40	24.40	32.80	35.40	39.60	42.60	44.90	50.50	52.70	56.70
Alluvial meadow soil	27.90	29.70	32.80	34.40	41.70	42.20	45.30	47.60	49.30	58.30	56.00	60.1
Brown soil	4.80	5.40	6.62	7.20	9.97	10.80	12.50	14.0	15.30	20.20	20.70	22.30

C. TRANSFER OF P APPLIED RECENTLY ADSORBED BY SOIL

In part A related to P adsorption this process has been studied through two laboratory procedures and then, the existence of two sites for adsorption was verified. In this part, the buffering capacity factor was mentioned because recently it has been considered by several soil workers as a good approach, when we require to evaluate P needs for a soil concerned with P fertilization.

Well, we have now considered that the knowledge we have concerned with the delivery of the P applied and adsorbed by a soil could help us to to define these soils better according to this element.

Syers et al 1970 (153) reported that the soils with a high phosphorus adsorption are those which transfer it less to the soil solution since these soils show a higher energy bound than the low P adsorption soils.

In order to verify this patterns, we have equilibrated these soils during 24 hours in 0.01 M calcium chloride medium that contains 8 ppm P as calcium diphosphate. This suspension was centrifuged, discarding this liquid and the residue soil was subjected to 14 consecutive extractions with water or 0.0.1 M calcium chloride solution in such a way as has been already described.

These P desorbed values obtained for water or 0.01 M calcium chloride extractions are included in tables 34 and 35 respectivaly.

In all soils, the values of table 34 were higher than those of table 35. That can be explained as a certain calcium solubilization produced by each water extraction.

TABLE Nº 34 : Values of P liberated by 14 water extraction expressed (in ppm P).

Soils	Nº extractions														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Total
Gypsum serosem	11.50	10.80	9.90	7.10	7.00	6.10	5.10	5.10	4.90	3.84	4.10	3.68	3.52	3.36	87.02
Marly serosem	15.90	7.60	5.70	4.90	4.30	4.30	4.30	4.30	4.30	3.52	2.80	2.24	2.24	2.24	68.64
Terrace soil	15.40	12.40	12.10	8.30	7.68	5.92	5.60	5.12	4.30	4.00	2.56	1.44	1.44	1.44	87.70
Alluvial soil	14.50	12.00	9.20	8.80	7.20	5.10	4.80	4.80	4.16	3.60	5.30	3.30	3.70	2.04	85.80
Brown soil	12.00	6.80	6.40	6.80	4.30	3.60	3.60	2.08	2.08	2.24	2.08	2.08	2.08	2.08	57.72

The P desorbed values obtained by 0.01 M Ca Cl_2 solution were chosen, because we believe that this 0.01 M Cl_2Ca medium simulates better the natural conditions for the calcareous soils and in order to establish a comparison between P adsorption and desorption P in these soils.

TBALE Nº 35: P values liberated by 14 extractions 0.01 M $CaCl_2$ (expressed in P ppm).

Soils	Number of extractions														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Total
Gypsum serosem	7.20	5.50	4.30	4.16	3.68	3.52	3.20	2.88	2.72	2.40	2.40	2.40	2.08	1.90	48.34
Marly serosem	9.76	3.20	2.90	2.70	2.70	2.70	2.70	2.70	2.70	1.90	1.60	1.60	1.28	1.28	39.72
Terrace soil	11.20	7.68	6.08	5.28	5.28	4.32	4.00	2.90	1.90	1.50	1.44	1.28	1.28	1.28	55.58
Alluvial meadow soil	11.50	6.40	4.40	3.60	3.60	3.60	2.70	2.70	2.40	2.40	2.40	1.92	1.60	1.48	50.70
Brown soil	6.80	3.40	3.40	3.40	1.76	1.76	1.60	1.44	1.44	1.44	1.28	1.28	1.28	1.28	31.56

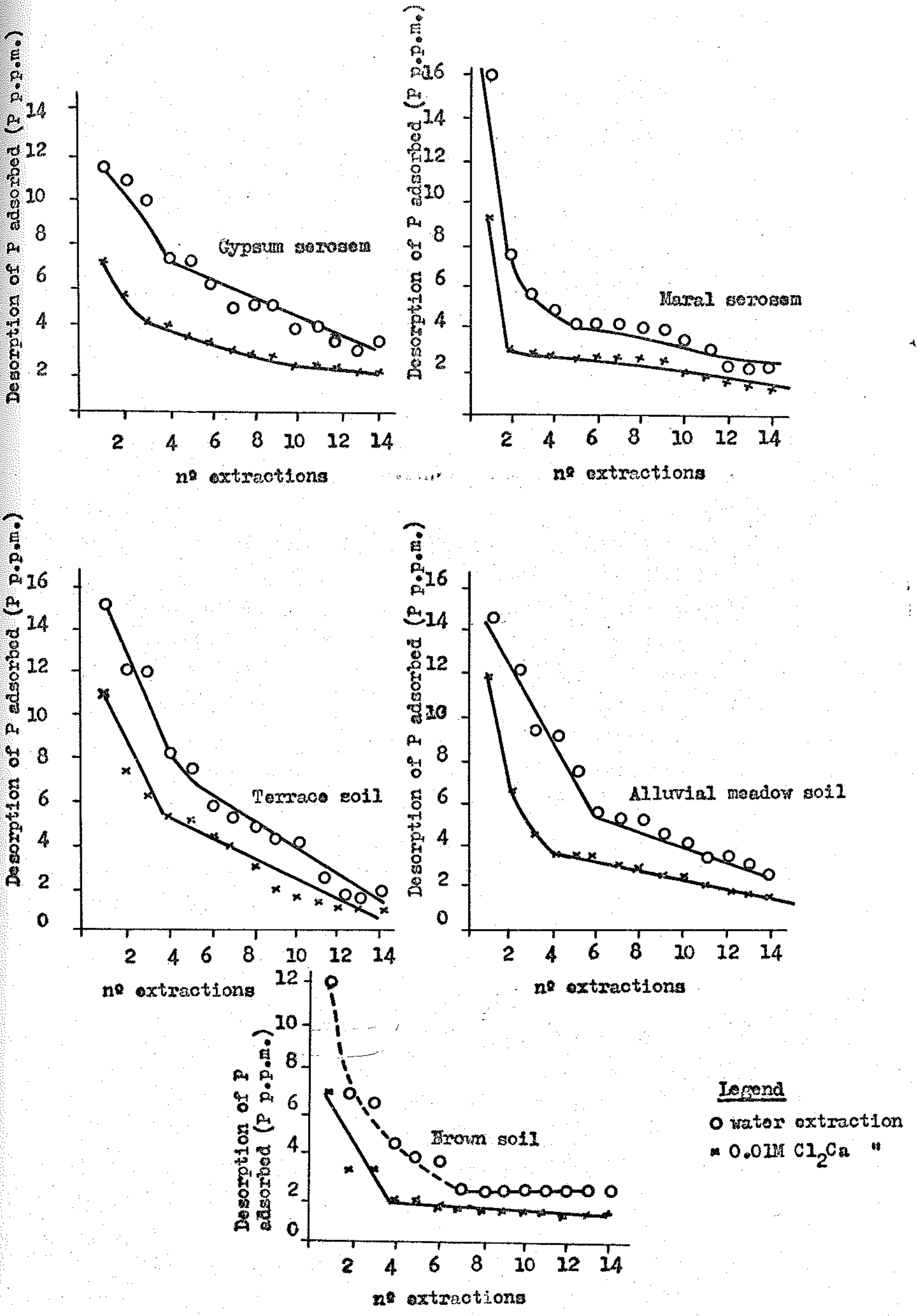
These P desorbed values by water action or 0.01 M calcium chloride solution have been drawn in graph 14 according to the number of extractions. By the shape of these curves it can be deduced that there are two areas of desorption according to the criterion of Blanchert 1964 (23), one corresponding to the P situated in the ionic atmosphere that sur ounded soil particles and the other is that related to P adsorbed on the surface of the soil particles. Brown soil, terrace soil and alluvial meadow soil exhibited there two well-defined areas, the former corresponding to the four extractions; from this fourth extraction it seems that the chemin desorption dominates. While in marly serosem this mechanism dominates and in gypsum serosem the two mechanisms are given simultaneously.

On the other handiif we express these total amounts of P desorbed (values table 35) as % of P adsorbed, we can observe:

Soils	P adsorbed (P ppm)	% of P liberated
Gypsum serosem	145	34
Marly serosem	124	32
Terrace soil	123	45
Alluvial meadow soil	155	32
Brown soil	68	46

Graph 14

Desorption curves of P added in the five soils



3.3. DYNAMICS OF THE PHOSPHORUS IN THE SOIL AND GROWTH OF THE PLANTS

In parts 3.1. and 3.2. it has been pointed out that there are differences among these five soils, related to P distribution along the soil profile, as well as connected to these physicochemical properties of adsorption and desorption of this nutrient.

Well, if by laboratory procedures we can confirm a differente pattern in these soils in relation to phosphorus, we believe that this behaviour can be reflected in a field of a crop grown under natural conditions in these soils. That led us to the conclusion of making use of greenhouse trials trials in which we made rye-grass grow under natural conditions for phosphorus (non P applied as fertilizers) and with a suitable supply in the other nutrients (please ses Methodology). Thus, a trial I was set up in the greenhouse, such as has been described on another page, and after these rye-grass plants had completed their vegetative cycle, they were harvested, weighed and analysed for phosphorus. Finding that there were differences in dry matter and P yield among these soils. That induced us to carry out a second trial on the same pots and under the same conditions used in trial I; once again, differences in dry matter and P yields were found. A sequence in these yields can be established.

Alluvial meadow soil > Terrace > Brown soil > Gypsum serosem > Marly serosem.

This sequence is slightly altered in trial II, and is as follows:

Terrace soil > Alluvial meadow soil > Marly serosem > Brown soil > Gypsum serosem.

These dry matter and P yields in roth the I and II trials are included in tables 36 and 37 respectively.

TABLE Nº 36: Dry matter and phosphorus yields in Trial I

Soils	Number of replications	Dry matter g/pot	% Phosphorus	Phosphorus yield in (mg P/pot)
Gypsum serosem	1	19.30	0.118	22.77
	2	21.80	0.114	31.39
	3	19.70	0.117	23.04
	4	22.75	0.128	29.12
	5	18.10	0.134	24.25
	6	21.15	0.120	25.38
				Average 25.99
Marly serosem	1	16.25	0.120	18.50
	2	17.20	0.120	20.64
	3	16.28	0.128	20.84
	4	15.40	0.130	20.02
	5	15.70	0.120	18.84
	6	16.18	0.120	19.42
				Average 19.71
Terrace soil	1	27.90	0.170	47.43
	2	24.40	0.170	41.48
	3	26.10	0.170	44.37
	4	23.25	0.169	39.29
	5	23.95	0.165	39.52
	6	26.15	0.178	46.55
				Average 43.10
Alluvial meadow soil from River Gállego	1	25.98	0.170	44.17
	2	25.25	0.170	42.93
	3	29.90	0.199	59.50
	4	29.30	0.199	58.31
	5	26.12	0.200	52.24
	6	25.90	0.179	47.36
				Average 50.75
Brown soil	1	22.00	0.142	31.24
	2	21.28	0.130	27.66
	3	17.00	0.118	20.06
	4	19.89	0.140	27.85
	5	19.83	0.143	29.36
	6	22.10	0.133	29.39
				Average 27.76

TABLE Nº 37: Dry matter and phosphorus yields in Trial II

Soils	Number of replications	Dry matter g/pot	% P	Phosphorus yield (mg P/pot)
Gypsum serosem	1	5.85	0.147	8.60
	2	4.80	0.177	8.50
	3	6.90	0.139	9.59
	4	5.60	0.189	10.19
	5	5.10	0.146	7.46
	6	5.00	0.141	7.05
				Average 8.57
Marly serosem	1	6.40	0.159	10.17
	2	6.90	0.180	12.42
	3	6.60	0.240	15.84
	4	7.43	0.186	13.82
	5	7.35	0.187	13.75
	6	6.00	0.194	11.64
				Average 12.94
Terrace soil	1	9.00	0.203	18.27
	2	10.20	0.232	23.66
	3	9.60	0.202	19.39
	4	9.80	0.222	21.76
	5	8.00	0.232	18.56
	6	10.50	0.192	20.16
				Average 20.30
Alluvial meadow soil from River Gállego	1	8.55	0.188	15.40
	2	10.05	0.197	19.50
	3	9.90	0.172	17.00
	4	9.45	0.194	18.30
	5	10.00	0.187	18.70
	6	9.30	0.181	16.83
				Average 17.62
Brown soil	1	6.60	0.180	10.80
	2	6.90	0.190	13.11
	3	6.50	0.175	11.38
	4	6.80	0.160	10.88
	5	6.10	0.176	10.73
	6	6.90	0.152	10.49
				Average 11.23

TABLE Nº 38

Variance analysis from phosphorus plant yield. (Trial I)

Source of variation	Sum of squares	degree of freedom	Mean square	F.
Replications	40.74	5	8.15	0.25
Soils	4242.00	4	1060.50	27.00 ++
Interaction	760.19	20	38.09	

++ highly significant at 5 and 1% levels.

Minimum significant difference $2.09 \times \frac{2 \times 38.09}{30} = 3.135$ mg P/pot.

TABLE Nº 39

Variance analysis for phosphorus yield obtained in Trial II

Source of variation	Sum of squares	degree of freedom	Mean square	F.
Replications	28.97	5	5.794	0.85
Soils	546.27	4	136.560	20.00 ++
Interaction	135.70	20	6.79	

++ highly significant at 5 and 1% levels.

Minimum significant difference $2.04 \times \frac{2 \times 6.79}{30} = 1.37$ mg P/pot.

This data was analysed through a variance study (please see tables 38 and 39), from which it can be deduced that P yields in each replication belong to the same population while those found in each soil are different and significant, showing in this way a different pattern exhibited by these soils in P dynamics.

In this part 3.3. we try to explain what is the cause of these different dry matter and P yields in this crop grown on these soils. We know that P adsorption by the plant will depend on the concentration of this nutrient in soil solution, for that reason we shall base our explanation on three ways:

a) How the inorganic P fractions contribute to the P adsorption by the plant.

b) How three quick laboratory assessments can evaluate these differences in P yields.

c) How the soil fertility factors have taken part in this P aupply to the plant.

A. SOIL P FRACTIONS

The P of soil solid phase is constituted by:

a) Organic P.
b) Inorganic P.

a) In part 3.1. we obtained information concerned with the total organic P, but we ignore which are the forms of this organic fraction because this fractionation was not carried out, as wall as their contents and susceptibility to mineralization, contributing, in this way, to P in the soil solution.

b) Inorganic phosphorus is formed by:

1) The soluble in ammonium chloride. It is considered as labil P due to its easy transfer to soil solution. These soils show the following range: (1.10 to 0.17 mg P/100 g soil) (values included in tables 14, 15,16,17 and 18).

2) That extracted by ammonium fluoride. This corresponds to phosphorus bounded aluminium and, according to the soil pH, it will have more or less soluble forms. Its content being in these five soils (3.10 to 0.75 mg P/100 g soil) (values included in tables 14,15,16, 17 and 18).

3) Soluble in sodium hydroxide. This fraction was present only in brown soil (2.32 mg P/100 g soil) (value included in table 18).

4) That extracted by sulphuric acid. It includes the whole series of calcium phosphate compounds, whose solubility is controlled by the soil pH and calcium free concentration that depends on the lime and gypsum presence and contents.

These five soils showed a range (20.12 to 3.87 mg P/100 g soil) (date from tables 14,15,16,17 and 18). In this inorganic P fraction it was verified that there exist P compounds included between hydroxyapatite and octocalcium phosphate.

The other fractions, such as soluble in reductant and occluded cannot be considered interesting with respect to soil fertility because a longer time is required for their solubilization.

At the end of the I and II greenhouse trials the mixtures (sand-soil) from pots without plants were taken up and soil from this mixture was separated by means of a 1 mm. sieve. In this soil material the fractionation for inorganic P was carried out according to the Chang-Jackson procedure. This data was included in tables 40 and 41.

TABLE Nº 40

Changes in the inorganic P fractions in soil semples after Trial I in the greenhouse. Data expressed in (mg P/100 g of soil).

Soils	P in $ClNH_4$		P in NH_4F		P in NaOH		P in H_2 SO_4	
	Initial	After	Initial	After	Initial	After	Initial	After
Gypsum serosem	0.96	1.00	0.75	4.00	0.086	0.00	14.00	14.00
Marly serosem	0.73	0.95	1.79	2.60	0.00	0.00	10.00	10.80
Terrace soil	1.10	1.86	2.28	2.60	0.00	0.00	18.11	18.60
Alluvial meadow soil	1.34	2.00	3.23	3.00	0.08	0.00	20.12	20.60
Brown soil	0.17	0.75	3.10	3.00	2.32	2.32	3.87	4.00

TABLE Nº 41

Changes in inorganic P fraction in soil samples after Trial II in the greenhouse. Data expressed in (mg P/100 a soil).

Soils	P in $ClNH_4$		P in FNH_4		P in NaOH		P in H_2 SO_4	
	Initial	After	Initial	After	Initial	After	Initial	After
Gypsum serosem	0.96	1.15	0.75	5.00	0.08	0.00	14.00	17.50
Marly serosem	0.73	1.00	1.79	5.00	0.00	0.00	10.00	14.50
Terrace soil	1.10	1.45	2.28	6.00	0.00	0.00	18.11	20.00
Alluvial meadow soil	1.34	1.75	3.23	6.20	0.08	0.00	20.12	24.50
Brown soil	0.17	1.25	3.10	4.40	2.32	2.32	3.87	6.00

In these tables 40 and 41, it can be seen that after the I and II greenhouse trials, the five soils showed a slight increase in their inorganic P fractions in relation to those obtained in the original soil samples. In these trials, phosphorus fertilization was not used, therefore we believe that these increases can be originated by a certain alteration of the organic fraction in these soil samples proceeding from non-plant pots of the I and II trials. This organic phosphorus alteration could have occured during these greenhouse assessments or during the drying of the mixtures (sand + soil) at room temperature during the Summer. The fact is that this organic phosphorus variation can be confirmed because the sum of these increases detected in inorganic P fractions is similar or higher than the increase obtained in these soil samples for P extracted by 6N or 2N H_2SO_4 (please see tables 42 and 43).

Table nº 42.- Transformations in organic phosphorus in soil samples after I greenhouse Trial. Values expressed in (mg P/100 g soil).

Soils	Sum of increases of inorg. P Fractions	P Soluble in 6N H_2SO_4		Organic P Mineralized	P Soluble in 2N H_2SO_4		Organic Mineralized.
		Initial	After		Initial	After	
Gypsum serosem	3.49	21.50	28.40	6.90	24.10	28.60	4.50
Marly serosem	1.23	15.48	21.60	6.12	15.01	21.00	5.99
Terrace soil	1.63	41.28	41.60	0.32	39.77	41.60	1.63
Alluvial meadow soil	1.15	40.40	41.00	0.60	37.88	40.00	2.12
Brown soil	0.71	17.20	17.60	0.40	15.90	16.60	0.70

Table nº 43.- Transformations in organic phosphorus in soil samples after II greenhouse Trial Data expressed in (mg P/100 g soil).

Soils	Sum of increases in inorg. P - fractions.	P soluble in 6N H_2SO_4		Organic P mineralized.	P soluble in 2N H_2SO_4		Organic P mineralized.
		Initial	After		Initial	After	
Gypsum serosem	7.84	21.50	28.00	7.50	24.10	27.00	2.90
Marly serosem	7.54	15.48	26.00	10.52	15.01	25.00	9.99
Terrace soil	5.97	41.28	46.00	4.72	39.77	45.00	5.23
Alluvial meadow soil	7.36	40.40	48.00	7.60	37.88	46.00	8.12
Brown soil	4.23	17.20	22.00	4.80	15.90	20.00	4.10

In order to Know what the contribution of these inorganic P fractions to the P adsorption by a crop is like, several soil workers - (Al-Abbas A.H. and Barber 1964 (2); Baldovinos F. 1966 (10); Grigg J.L. 1965 (66); Hanatiaux G. 1966 (75); Khanna J.K. 1967 (94); Payne H. and Hanna 1965 (127); Pratt P.F. and Garber M.J. 1964 (131); Sharma D. et al 1963 (141); Singh N. et al 1968 (143); Susuki et al 1963 (149) have used correlation procedures between the P yield of a content of these inorganic P fractions.

In our case, in table 44 this correlation between the yield (in Trial I as total (I + II P y yield) related to the content of these inorganic.fractions has been reflected.

Table nº 44.- Correlation coefficiente (r), regression equations between P yield rye-grass and content of these inorg. P fractions.

Inorg. P fractions	P yield rye-grass (I Trial)		Total P yield rye-grass	
	r	regression equation	r	regression equation
P in $Cl\,N\,H_4$	0.93	$y = 5.91 + 0.84\,x$	0.94	$y = 2.20\,x - 25.01$
P in $N\,H_4F$	0.38		0.20	
P in H_2SO_4	0.54		0.70	
P in (x) H_2SO_4	0.86		0.90	

(x) For calcareous soils.

In both cases of P yield, the P solution in ammonium chloride contributes significantly (r = 0.93 and 0.94) to this P adsorption by rye-grass. While the fraction extracted by sulphuric acid did not show itself to be significant in all soils (r = 0.54 and 0.70); however, when the date of calcareous soils was included, these correlation coefficients become significant, showing us that in these calcareous, in a not very long period of time, this P fraction will contribute to this phosphorus supply to plants.

B) Estimation through quick laboratory assessments recommended for phosphorus assimilable by plants.

Normally, in soil laboratories, there are quick methods which, in a short period of time, supply information concerning phosphorus assimilable by plants. For this purpose, a great number of extracting solutions have been used, believing that each of them can carry out a suitable estimation of this soil phosphorus absorbed by plants.

In this study three of these extracting solutions, Van de Paaw, Sissngh, Olsen and Burriel-Hernando, have been considered; because the first, in a preceding study, has reflected this situation (Eleizalde M.B. and Van diest A. 1971 (48); the Olsen method is wisely used for calcareous soils and the Burriel-Hernando procedure is followed at most soil laboratories in Spain.

TABLE 45: Soil P extracted by the Van der Paaw - Sissinhg method. Data expressed in (mg P/100 g soil)

Soils	Initial soil samples	Soil samples after I greenhouse trial	Soil samples after II greenhouse trial
Gypsum serosem	0.41	0.59	0.38
Marly serosem	0.35	0.45	0.33
Terrace soil	0.65	0.77	0.73
Alluvial meadow soil	0.76	1.01	0.77
Brown soil	0.35	0.66	0.45

TABLE Nº 46: Soil P extracted by the Olsen method, expressed in (mg P/100 g soil.

Soils	Initial soil samples	Soil samples after I greenhouse trial	Soil samples after II greenhouse trial
Gypsum serosem	2.56	3.26	3.00
Marly serosem	2.36	2.76	2.76
Terrace soil	3.12	4.00	4.00
Alluvial meadow soil	2.10	4.40	4.40
Brown soil	0.10	1.26	1.00

TABLE Nº 47: Soil P extracted by the Burriel-Hernando solution, expressed in (mg P/100 g soil).

Soils	Initial soil samples	Soil samples after I greenhouse trial	Soil samples after II greenhouse trial
Gypsum serosem	3.01	4.26	6.20
Marly serosem	0.69	1.29	4.50
Terrace soil	2.15	2.41	6.50
Alluvial meadow soil	1.72	3.18	6.50
Brown soil	2.06	2.50	6.40

In tables 45, 46 and 47 there can be seen the data of phosphorus extracted according to these methods in soil samples before the I and II greenhouse trials, as well as those corresponding to bottrials taken up from non plant pots. For the three extracting solutions, an increase in phosphorus content from soil samples from non plant pots of the I and II greenhouse trials was observed. These phosphorus contents in the soil samples obtained by these extracting solutions were correlated separately with the rye-grass phosphorus yield (trial I) and the total phosphorus yield of rye-grass. That can be appreciated in table 48.

TABLE 48: Correlation coefficients (r), regression equation between soil P extracted by these solutions and P yield of rye-grass.

Soil P extracted by	P yield rye-grass at I trial		Total P yield of rye-gras	
	r		r	
Olsen	0.65	—	0.73	—
Van der Paaw Sissingh	0.97++	y=2.38x-7.95	0.99++	y=4.90+3.20x
Burrel Hernando	0.25	—	0.60	—

++ highly significant at 1% and 5% levels.

From this table 48, we deduce that of the three extracting solutions, that corresponding to Van der Paaw-Sissinhg carried out a suitable estimation of P absorbed by rye-grass. While the other two solutions (Olsen and Burriel-Hernando) supplied low and non significant correlation cooficients ($r = 0.65$ and 0.25) at trial I. These solutions increased their correlation values with total phosphorus yield ($r = 0.73$ and 0.60) showing in this way that these extracting solutions have preferably acted on phosphorus forms, which have a slow transfer to the soil solution.

In order to verify this, the fractioning of inorganic P according to the Chang-Jackson procedure in soil samples of both trials after the action of these extracting solutions was carried out.

In tables 49 and 50, the contents of these P fractions before and after the action of these extracting solutions are included. The differences between both contents in these inorganic P fractions will reflect the P removal from these inorganic P fractions by the action of these Olsen and Burriel-Hernando procedures.

TABLE Nº 49 : Influence of Olsen solution in inorganic P fractions. Data expressed in mg P/100 g soil

Soils	Soil samples from I Trial						Soil samples from II Trial					
	P in Cl NH_4			P on $H_2 50_4$			P in Cl NH_4			P in H_2 SO_4		
	Initial	After	Dif.	Initial	After	Dif.	Initial	After	Dif.	Initial	After	Dif.
Gypsum serosem	1.00	0.90	0.10	14.40	13.30	1.10	1.15	1.10	0.05	17.50	15.60	1.9
Marly serosem	0.95	0.80	0.15	10.80	8.00	2.80	1.00	0.97	0.03	14.50	14.00	0.5
Terrace soil	1.86	1.70	0.16	18.60	16.60	2.00	1.15	1.10	0.05	20.00	18.00	2.0
Alluvial meadow soil	2.00	1.80	0.20	20.60	18.60	2.00	1.75	1.30	0.45	24.50	22.00	2.5
Brown soil	0.75	0.60	0.15	4.00	3.00	1.00	0.75	0.70	0.05	6.00	3.80	2.2

Note: The values that appear in Initial correspond to the After column in tables 40 and 41.

In this table the After column means the data obtained of the inorganic P fractionalization in soil residue in which P was extracted before by this Olsen method.

TABLE Nº 50: Influence of the Burriel-Hernando procedure on the soil P fractions. Data expressed in (mg P/100 g soil).

Soils	Soil samples from I Trial P in Cl NH_4 Initial	 After	 Dif.	 P in H_2 SO_4 Initial	 After	 Dif.	Soil samples from II Trial P in Cl NH_4 Initial	 After	 Dif.	 P in H_2 SO_4 Initial	 After	 Dif.
Gypsum serosem	1.00	0.72	0.28	14.80	11.50	3.30	1.15	1.05	0.10	17.00	10.00	7.00
Marly serosem	0.95	0.56	0.39	10.80	9.00	1.80	1.00	0.95	0.05	14.50	11.00	3.50
Terrace soil	1.86	0.86	1.00	18.60	16.00	2.60	1.15	1.05	0.10	20.00	15.50	4.50
Alluvial meadow soil	2.00	1.20	0.80	20.60	18.96	1.04	1.75	1.15	0.60	24.50	20.00	4.50
Brown soil	0.75	0.32	0.43	4.00	3.50	0.50	0.75	0.65	0.10	6.00	5.50	0.50

Note: The data included in the Initial column is that of the After column in tables 40 and 41. In this table the values in After means the data of these fractions obtained in the soil residue in which P soil was extracted before by Burriel-Hernando solution.

In table 51 can be seen the correlation of these differences related to soil P extracted by these solutions.

Through the correlation coefficients obtained we deduce that the Olsen procedure has a greater influece than the Burriel-Hernando method on the P soluble in Cl NH_4 and that both extractin solutions acted significatively on the Ca-P fraction.

TABLE Nº 51 : Correlation between soil P extracted by the Olsen and Burriel-Hernando solutions in relation to their influence on the P soluble Cl N H_4 and P- Ca.

Extracting solution	P in Cl N H_4		P in H_2 SO_4	
	r	regression equation	r	regression equation
Olsen	0.56	——	0.63+	$y=1.29 + 0.77\ x$
Burriel-Hernando	0.53	——	0.73+	$y=1.53 + 0.91\ x$

+ Significant at 5% level.

C. Through the soil fertility factors.

It was mentioned before that the phosphorus absorption by the plant depends on the concentration of this nutrient in soil solution. This concentration being governed by the rate of P transfer from solid phase to soil solution.

This can be summarized in the following scheme proposed by Fried and Shapiro 1967 (57), confirmed by Cooke and Larsen 1970 (102) and Guany and Sutton 1967 (67).

P in solid phase ⟶ P in soil solution ⟶ P in neighbourhood roots ⟶ P in plant

From this scheme we deduce:

1) There is a phosphorus transfer from the solid phase to the soil solution, being involved, in this process all the labil P forme; that is to say, the quantity factor. Among those forms the P surface and certain compounds in the inorganic P fractions can be considered, which according to their water solubility can be contributed to P in the soil solution.

2) P in soil solution through a diffusion process will move to the neighbourhood of roots. There must be suitable physical conditions such as humidity, good soil particle aggregation, etc., in order to facilitate on the one hand the diffusion of this nutrient and on the other hand a good root development.

3) The absorption of this nutrient by the plant will depend on the requirements proper to its species, age and physiological state.

Therefore, we can say that the soil phosphorus supply to a plant depends on the concentration of this nutrient at a given time in soil solution (intensity factor) and which is controlled by the rate of P transfer from the solid phase to the soil solution (desorption rate), that is controlled by the total quantity of P labil (quantity factor) that the soils have.

These factors that take place in the phosphorus supply to the plant have been evaluated through laboratory methods such as:

Intensity factor

Phosphorus soluble in one water extraction	Fried et al.
" " in 0.01 M $CaCl_2$...............	Schofield et al
P adsorbed by anionic resin at short equilibrium time	A. Van Diest.

Quantity factor

Total maximum P adsorption	Hagin et al.
% saturation P	Rennie et al.
Maximum P adsorption at low sites of adsorption	Fried et al.
Total amount of P desorbed	Fried et al.
P adsorbed by anionic resin at long equilibrium time	A. Van Diest.

The values of these fertility factors estimated by the laboratory procedures mentioned have been included in Table 52.

TABLE Nº 52 : Values of the intensity and quantity factors, expressed in (P p.p.m.)

Soils	Intensity			Quantity							
	Water	0.01 M $CaCl_2$	Resin at 1 hour	KH_2PO_4		$Ca(H_2PO_4)$		% sat+		Resin	Sum 14 water extract
				K_2	K_2 in 1 site	K_2	K_2 in 1 site	1º	2º	r=72 h	
Gypsum serosem	0.616	0.029	11.200	322	97	225	114	24	16	37.60	7.87
Marly serosem	0.700	0.022	4.400	207	88	143	143	45	28	21.50	6.77
Terrace soil	0.768,	0.029	16.120	211	70	190	143	61	30	51.60	15.38
Alluvial meadow soil	1.040	0.043	30.300	238	106	187	117	69	59	54.80	16.3
Brown soil	0.700	0.022	2.200	55	51	44	44	31	36	24.00	7.08

Note: + : % saturation was calculated as P surface related to the maximum P adsorption at I site. (1º and 2º) means according to both laboratory procedures used by P adsorption.

From this data in table 52, these soils can be classified in:

1) Soils with low intensity factor (brown soil and marly serosem).

2) Soils with moderate intensity factor (gypsum serosem and terrace soil).

3) Soil with high intensity factor (alluvial meadow soil).

In relation to the quantity factor.

The soils studied can be goruped into

1) Low-moderate quantity factor. (brown soil, gypsum serosem and marly serosem).

2) A high quantity factors. (terrace soil and alluvial meadow soil).

In order to verify this classification, we have followed the criterion of S.R. Williams 1967 (174) in which this soil worker estimates the intensity factor against dry matter yield and the quantity related to phosphorus plant yield.

Thus, in table 53, we observe that among all the laboratory methods used, the anionic resin at a 1 hour time well reflects the difference concerning this factor among these soils.

TABLE Nº 53: Correlation between dry matter yield and values of intensity factor

Value	Dry matter yild in I trial	Total dry matter yield
Water	0.74	0.77
0.01 M Cl_2 Ca	0.81	0.89+
Resin at 1 hour	0.88 +	0.92 ++

+ significant at 5% level – ++ significant at 5% level and 1% level.

In relation to the quantity factor, it has been well defined under these experimental greenthouse conditions, by the total amount of P desorbed by 14 water extractions and by the anionic resin method at 72 hours; due to both procedures having been significatively correlated with the phosphorus yield (blease see table 54).

The other laboratory methods, such as total maximum P adsorption and that corresponding to the I site, under these experimental conditions (no P fertilizer used), did not evaluate this factor. However, if we used the % saturation (P surface related to maximum P adsorption at the I site) there was a tendency to show a significant correlation with P yield; that means that this approach can be useful in the estimation of this quantity factor.

TABLE Nº 54: Correlation between P yield and quantity factor

Quantity factor	Phosphorus yield in I Trial	Total P yield
Total maximum P adsorption according $KH_2 PO_4$	0.15	0.16
K_2 in I site ($KH_2 PO_4$ method)	0.14	0.49
Total K_2 according $Ca (H_2PO_4) 2$ method)	0.21	0.19
K_2 in I site according $Ca (H_2PO_4)2$	0.19	0.28
% saturation	0.81 0.73	0.88+ 0.71
Sum of M. water extractions	0.97++	0.98++
Resin at 72 h.	0.92++	0.89++

highly significant at 5 and 1% level.

How can we explain the difference exhibited by these soils in phosphorus yield at the I Trial?

Initially, we believe that the different P concentrations in soil solution (intensity factor) showed by these soils, influenced these different yields, although this difference was not so marked between two soils such as terrace soil and alluvial meadow soil because they have similar quantity and desorption rate factors. In the other soils, it can be said that this phosphorus absorption was regulated by the simultaneous action of three factors (intensity, quantity and rate of P desorption). This latter factor being that which has significantly marked this difference of phosphorus yield obtained in these soils (please see table 55).

In trial II there was a decrease in crop yield compared to that exhibited in trial I. These yields in trial II being approximately 67, 49, 34 and 33% of the initial obtained in trial I for marly serosem, terrace soil, brown soil, alluvial meadow soil and gypsum serosem respectively.

This can perhaps be explained because these soils, under natural conditions, had different values of quantity factor and that the buffering capacity factor calculated in range 0.5 to 0.6 P ppm in final solution (see page. 119) was also different.

Thus, in marly and gypsum serosems which have different intensities, proximate quantities that become similar and rate of P desorption, but different buffering capacities, this decrease of yield observed in trial II can be attributed to the gypsum serosem showing a tendency to have a higher energy of phosphorus adsorption than marly serosem, and, as a consequence, a lower phosphorus supply to the soil solution.

Brown soil held its rye-grass yield in trial II at 40% in relation to trial I. This soil compared with the above group, presents lower intensity and quantity factors although a similar P desorption rate. In relation to time, it becomes more easily depleted than the above group, although there will be required a lesser P amount of fertilizer, it being necessary that this dressing be continued in order to get suitable yields.

In terrace soil and alluvial meadow soil from the River Gállego it can be seen that they have, under natural conditions, a similar quantity factor. These soils have held their yield in trial II at about 47 and 33% respectively.

It was mentioned before that the difference of P yield in trial I was, to a great extent, due to the different intensity factors shown by these soils. Therefore, there exists a lower % yield in alluvial meadow soil than terrace soil. Under a phosphorus dressing the former will require a lesser amount of P fertilizer than the latter for an optimum yield.

Marly serosem and terrace soil show different intensities, quantities and P desorption rate as well, as reflecting different yields in the I and II trials; however, there exists a tendency that in trial II the yield obtained becomes similar in both soils. Under phosphorus fertilization, marly serosem will require a slightly higher amount of P than terrace soil due to this soil showing a higher energy for P adsorption than the latter. As well, the P desorption % (page. 138) was lower than the terrace soil due to the predominance of the chemical sorption mechanisms.

In these soils there was a significant ratio between total P yield and rate of P desorption.- (Please see table 55).

TABLE Nº 55 : Correlation coefficient (r) and regression equation between P yield and rate of P desorption in these soils.

P yield in Trial I		Total P yield	
r	regression equation	r	regression equation
0.96++	y= 7.98 + 33.53 x	0.98++	y= 13.50 + 44.85 x

++ highly significant at 5 and 1% levels.

CHAPTER 4

CONCLUSIONS
CONCLUSIONS
CONCLUSIONES

CHAPTER 4

CONCLUSIONS

1.- The total phosphorus distribution along soil profile is influenced by the organic phosphorus content in the different soil horizons.

2.- The total organic phosphorus shows the same tendency in its distribution than that exhibited by organic matter content in the different soil horizons.

3.- In the four calcareous soils, the dominant fraction of inorganic phosphorus is the bound to calcium, which content is similar in all soil horizons.

4.- The amount of P - Al extracted depends upon pH of the 0.5.N. ammonium fluoride solution.

5.- In brown soil, the dominant fraction of inorganic phosphorus is the - soluble in reductant, which is constant along this soil profile.

6.- To calculate the weathering degree of brown soil, the P fraction soluble in reductant must be included together with other inorganic P - fraction in a scheme.

7.- Pca is formed by compounds included between hydroxiapatite and octocalcium phosphate.

8.- The studies concerned to P sorption must be carried out in presence of calcium chloride and increased amounts of calcium diphosphate.

9.- The Langmuir modified equation for calculating K_1 and K_2 values must be followed.

10.- In three soils (gypsum serosem, maral serosem and brown soil). The liberation of P from solid phase to soil solution is governed by - the solubility of P compounds while in the other two calcareous ones is a typical desorption process.

11.- The five soils have different values of P desorption rate.

12.- In all these soils exist a moderate reaction of P desorption, which is refected by the anion resin procedure.

13.- The % of liberation of P adsorbed, depends upon the quantity adsorbed, constant bound P to soil, and mechanism by which this P adsorption has been produced by soil.

14.- Among the inorganic P fractions, those solubles in ammonium chloride and in sulphuric and have intervened in the phosphorus supply to rye-grass grown on these five soils.

15.- From three laboratory procedures used by the estimation P available, only the of Van der Paaw-Sissingh has well reflected the soil P absorbed by rye-grass.

16.- Intensity factor is well evaluated by soil P extraction according - Anionic resin method at t = 1 hour and the quantity factor equals to the sum of soil P extracted by 14 water extractions and that taken by an anionic resin procedure at 72 hours.

17.- The phosphorus supply is governed simoulstlly by the intensity, quantity and rate desorption factors in gypsum serosem, Maral serosem - and Brown soil.

18.- The difference in rye-grass yield between terrace soil and alluvial meadow soil from Gállego River can be attributed to intensity factor.

19.- The decreasing in plant yield observed in a subsequent trial, is due to a different values, which are exhibited by the quantity and capacity factors.

CHAPITRE 4

CONCLUSIONS

1.- La distribution du phosphore total est influencée par le contenu en phosphore organique des différents horizons.

2.- Le phosphore organique total présente la même tendance dans sa distribution dans les cinq sols étudiés qui coincide avec le contenu de matière organique dans ces sols.

3.- Dans les quatre sols calcaires, la fraction dominante du phosphore - inorganique, est celle liée au calcium dont le contenu se maintient similaire dans les horizons de ces sols.

4.- La quantité du P - Al extraite dépend du pH de la solution 0.5N de fluorure d'ammonium.

5.- Dans la terre brune, la fraction dominante du phosphore inorganique, est la soluble en reductant qui est constante tout au long du profil.

6.- Pour valorer le degré de météorisation de la terre brune on doit avoir présente la fraction soluble du réductant.

7.- La fraction de phosphate de calcium est formée par des composés inclus entre l'hydroxiapatite et le phosphate octocalcique.

8.- Les études sur retention de phosphore doivent se réaliser en présence du chlorure calcique et en quantités croissantes de phosphate monocalcique.

9.- L'équation modifiée de Langmuir pour calculer les valeurs K_1 et K_2 doit être considérée.

10.- Dans trois sols (serosen plâtreux, serosem margueux et terre brune) la libération de phosphore à la solution est gouvernée par la solubilité des composés de phosphore; tandis que dans les autres deux sols calcaires c'est une désorption typique.

11.- Les 5 sols considérés présentent des valeurs différentes de taux de cession.

12.- Dans tous ces sols il existe une réaction modérée de libération de phosphore comme l'indique le méthode de la résine anionique.

13.- Le pourcentage de libération du phosphore adsorbé, dépende de la quantité adsorbée, constante d'union P au sol, et mécanisme pour lequel il s'est produit cette adsorption du phosphore pour le sol.

14.- Entre les fractions du phosphore inorganique, les solubles en chlorure d'ammonium et en acide sulphurique interviennent dans la fourniture de phosphore à l'avoine fourragère qui a grandi dans ces 5 sols.

15.- Des trois procès de laboratoire usés pour le phosphore assimilable, seul celui de Van der Paaw-Sissing estima adécuatement le phosphore absorbé pour l'avoine fourragère.

16.- Le facteur d'intensité est bien refleté avec l'extraction du P par la résine anionique pendant 1 heure et le facteur quantité équivaut à l'addition du P extrait en 14 extractions consécutives avec eau et à l'extrait par résine anionique pendant 72 heures.

17.- La fourniture de phosphore est régulée simultánément par les facteurs intensité, quantité et taux de cession dans les sols serosem plâtreux, serosem margueux et terre brune.

18.- La différence en rendement entre 2 sols (brun calcaire sur terrace et vega du Fleuve Gállego) peut être attribué au facteur intensité.

19.- La diminution de rendement observée dans une culture subsuivante, - est due aux différentes valeurs que présentent les facteurs quantité et capacité.

CAPITULO 4

CONCLUSIONES

1.- La distribución des fosforo total está influenciada por el contenido de fosforo orgánico de los distintos horizontes.

2.- El fosforo orgánico total presenta la misma tendencia en su distribución en los cinco suelos estudiados que coincide con el contenido de materia orgánica en estos suelos.

3.- En los cuatro suelos calizos, la fracción dominante del fosforo inorgánico, es la ligada al calcio cuyo contenido se mantiene similar en los horizontes de estos suelos.

4.- La cantidad de P - Al extraida depende del pH de la solución 0.5N de fluoruro de amonio.

5.- En la tierra parda, la fracción dominante del fosforo inorgánico es la soluble en reductante que es constante a lo largo del perfil.

6.- Para valorar el grado de meteorización de la tierra parda debe tenerse presente la fracción soluble en reductante.

7.- La fracción de fosfato de calcio está formada por compuestos incluidos entre el hidroxiapatito y el fosfato octocálcico.

8.- Los estudios sobre retención de fosforo deben realizarse en presencia de cloruro cálcico y cantidades crecientes de fosfato monocálcico.

9.- La ecuación modificada de Langmuir para calcular los valores K_1 y K_2 debe tomarse en cuenta.

10.- En tres suelos (Serosem yesoso, serosem margoso y tierra parda) la liberación de fosforo a la solución está gobernada por la solubilidad de los compuestos de fosforo; mientras que en los otros dos suelos calizos es una desorción típica.

11.- Los cinco suelos considerados presentant valores distintos de tasa de cesión.

12.- En todos estos suelos existen una reacción moderada de liberación de fosforo como lo señala el metodo de la resina aniónica.

13.- El % de liberación del fosforo adsorbido, depende de la cantidad adsorbida, constante de unión P al suelo, y mecanismo por el cual se ha producido esta adsorción de fosforo por el suelo.

14.- Entre las fracciones del fosforo inorgánico, las solubles en cloruro de amonio y en ácido sulfurico intervienen en el suministro de fosforo al centeno forrajero crecido en estos cinco suelos.

15.- De los tres procedimientos de laboratorio usados para el fosforo asimilable, solo el de Van der Paanw-Sissingh estimo adecuadamente el fosforo absorbido por el centeno forrajero.

16.- El factor intensidad está bien reflejado con la extracción del P por resina aniónica durante 1 hora y el factor cantidad equivale a la suma del P extraido en 14 extracciones consecutivas con agua y al extractado por resina aniónica durante 72 horas.

17.- El suministro de fosforo está regulado simultaneamente por los factores intensidad, cantidad y tasa de cesión en los suelos serosem yesoso, serosem margoso y tierra parda.

18.- La diferencia en rendimiento entre dos suelos (pardo calizo sobre terraza y vega del río Gállego) puede atribuirse al factor intensidad.

19.- La disminución de rendimiento observada en un cultivo subsiguiente, es debida a los valores diferentes que presentan los factores cantidad y capacidad.

CHAPTER 5

GENERAL CONSIDERATIONS
CONSIDERATIONS GENERALES
CONSIDERACIONES GENERALES

CHAPTER 5

GENERAL CONSIDERATIONS

According to the above conclusions, we can see that the phosphorus behaviour in these soils shows a wide and complex panorama, since we have found that the organic phosphorus has presented values so high that we did not expect them. Thus, this P fraction can be interesting in plant - nutrition, after its mineralization is produced. That will demand from us a further and more detailed study related to the forms included in this phosphorus fraction as well as with regard to the susceptibility show for the mineralization process.

Among the inorganic phosphorus fractions, it has been seen that the solubles in ammonium chloride and sulphuric acid influenced being an immediate supply of P in soil solution and that bound to calcium in these calcareous soils according to their pH, means that they are slow soluble P forms, reflecting in this way their slow availability to plants.

Under the natural conditions that these soils were at in the I and II trials (no P fertilizer applied), it was observed that the phosphorus yield at trial I was governed simultaneously by the intensity, quantity and rate of P desorption factors. In two soils (terrace soil and alluvial meadow soil) it can be said that the initial phosphorus concentration in soil solution (intensity factor) was responsible for the difference in yields exhibited by both soils.

In the other soils it can be believed that the phosphorus absorption by the plant was controlled by the three soil fertility factors considered.

In trial II, a decrease in phosphorus yield was observed; that was more marked in some soils than in others. In this case, we have tried to explain this fact that was due to the different quantity and buffering -

capacity factors shown by these soils. For phosphorus plant yield in trial I and, as well, the total phosphorus yield, there has existed a significant correlation with the rate of P desorption in these soils.

These situations shown in both greenhouse trials can be produced under land conditions although they will not be so marked. Thus, if we intend in the future to carry out an evaluation concerning the requirements of these soils in this nutrient, we must take these soil fertility factors into account.

At the present time, in ivestigation there exists the tendency to use adsorption isotherms which can integrate in a single value all these soil fertility factors such as the expression recommended by Fox and Kamprath 1.970 (52).

Other soil workers such as Ozanne et al. 1.968 (124) and Rajan S.S. 1.973 (133) point out that a certain phosphorus concentration in final solution is enough for the estimation of the soil requirements related to optimum crop yield.

Both considerations seem to us to be useful for an evaluation fo soil requirements in phosphorus fertilization.

In the calcareous soils studied, they have clse values of maximum P adsorption in site I and then, the application of certain amounts of P equivalent to 0-1 P p.p.m. in final solution in these soil, will allow us to have them in suitable conditions to appreciate exactly at which P conce tration in final solution the maximum yield is reached. Afterwards, using this buffering capacity factor, one can establish a more precise criterion regarding the validity of P estimation by the Burriel Hernando and Olsen extracting solutions through multiple correlation procedures.

For calcareous and non calcareous soils, it would be more advisable to use the expression recommended by Fox and Kamparth, since it can occur that in this case an optimum crop yield would be obtained at different P concentrations.

CHAPITRE 5

CONSIDERATIONS GENERALES

D'après les conclusions obtenues par cette étude nous voyons que le comportement du phosphore dans ces sols, sous un point de vue de fertilité, offre un ample et complexe panorama, étant donné que nous nous sommes trouvés que le phosphore organique a présenté des valeurs qu'on n'attendait pas. Pour tant, cela peut être une fraction d'intérêt après se minéraliser dans la nutrition de la plante. Ceci nous exigera une étude postérieure plus détaillée sur les formes où il se présente ainsi que la susceptibilité qu'ont à se minéraliser.

Entre les fractions de phosphore inorganique, on a vu que les solubles en chlorure d'ammonium et en acide sulphurique influrent sur le phosphore absorbé par l'avoine fourragère qui grandit sur ces sols. Etant la première façon d'une exploitation immédiate, tandis que celle liée au calcium dans les sols calcaires due au pH qu'ils ont, il s'agit de composés peu solubles, reflétant ainsi sa lente disponibilité pour les cultures.

Sous les conditions expérimentales que furent ces sols dans les essais I et II en serre, on ne leur applica pas de phosphore et on observa que le rendement de l'avoine fourragère dans l'essai I fut régulée simultanément par les facteurs (intensité, quantité et taux de cession). Dans deux sols (Terrace et vega du fleuve Gállego) on peut dire que la concentration initiale du phosphore dans la solution du sol (facteur intensité) fut responsable de la différence en rendement obtenue entre ces deux sols. Dans les autres trois sols étudiés, la différence en rendement on peut prévoir qu'elle soit à l'action conjointe des trois facteurs de fertilité considérés.

Dans l'essai II, on observa una diminution dans le rendement de l'avoine fourragère qui fut plus intense dans un sol ou autres. Dans ce cas nous avons traité d'expliquer cette diminution et qui fut due au facteur quantité et capacité d'adoucissement que présentent ces sols.

Ainsi que pour le rendement de phosphore dans l'essai I comme pour le rendement total de phosphore, il existe une correlation hautement significative avec le taux de cession que présentent ces sols.

Les situation qui se sont présentées dans les essais I et II en serre, se donnent aussi au champ quoiqu'elles ne soient pas aussi considérables. Pourtant, si nous avons l'intention dans un futur immédiat de faire une évaluation des exigences de ces sols de ce nutriment, nous devons - avoir présent ces facteurs de fertilité.

Actuellement dans la recherche il existe la tendance d'employer des Isothermes d'adsortion qui peuvent intégrer dans une seule valeur, tous ces facteurs comme l'expression recommendée par Fox et Kampath 1.970 - (48); Khasaw meth F.E et J.P. Copeland 1.973 (95).

D'autres chercheurs comme Ozanne et al. 1.968 (124); Rajan S.S. 1.973 (133), indiquent qu'une concentration donnée du phosphore dans la solution finale, est suffisante pour l'estimation des exigences dans un sol pour le rendement optimum d'une culture.

Ces deux critères nous paraissent précieux pour une évaluation des exigences dans un sol en fertilisation phosphatée.

Dans ces sols calcaires étudiés qui ont des valeurs très proches d'adsorption de phosphore du lieu I, en appliquant des quantités de phosphore dans la ligne équivalente (0-1 p.p.m. P dans la solution finale) nous permettra de les avoir dans des conditions adécuates pour déterminer avec - exactitude à qu'elle ligne de concentration de phosphore dans la solution finale, on obtient le rendement maximum et en employant cette expression de facteur de capacité, on peut établir un critère plus exact sur la vali dité de l'estimation que fassent du phosphore assimilable les solutions d'extraction, Olsen et Burriel Hernando.

Pour établir les exigences de ce nutriment entre sols calcaires et non calcaires peut être qu'il sera plus effectif d'employer l'expression recommandée par Fox-Kampath et Khasawneth F.E. et L.P. Copeland, que dans une valeur incluent tous les facteurs de fertilité considérés, étant donné qu'il peut se produire le cas où on obtient le maximum de rendement - dans une culture à différentes concentrations de phosphore dans la solution finale.

CAPITULO 5

CONSIDERACIONES GENERALES

Por las conclusiones obtenidas de este estudio vemos que el comportamiento del fósforo en estos suelos, bajo un punto de vista de fertilidad, ofrece un panorama amplio y complejo, ya que nos hemos encontrado con que el fósforo orgánico ha presentado valores que no esperábamos. Por tanto puede ser una fracción de interés después de mineralizarse en la nutrición de la planta. Esto nos exigirá un estudio posterior más detallado sobre las formas en que se presenta asi como la suceptibilidad que tienen a mineralizarse.

Entre las francciones de fósforo inorgánico, se ha visto que las solubles en cloruro de amonio y en ácido sulfúrico influyeron sobre el fósforo absorbido por el centeno forrajero que crecio en estos suelos. Siendo la primera forma de un aprovechamiento inmediato, mientras que la ligada al calcio en los suelos calizos debido al pH que tienen, se tratan de compuestos poco solubles, reflejando asi su lenta disponibilidad para los cultivos.

Bajo las condiciones experimentales que estuvieron estos suelos en los ensayos I y II de invernadero, de no aplicación de fósforo, se observó que el rendimiento del centeno forrajero en el ensayo I estuvo regulado simultaneamente por los factores (intensidad, cantidad y tasa de cesión). En dos suelos (terraza y vega del río Gállego) puede decirse que la concentración inicial del fósforo en la solución del suelo (factor intensidad) fué responsable de la diferencia en rendimiento obtenido entre ambos suelos. En los otros tres suelos estudiados, la diferencia en rendimiento puede preveerse que sea a la acción conjunta de los tres factores de fertilidad considerados.

En el ensayo II, se observó una disminución en el rendimiento del centeno forrajero que fué más señalada en unos suelos que en otros. En este caso, hemos tratado de explicar este descenso que fué debido al factor cantidad y capacidad de amortiguación que presentan estos suelos.

Tanto para el rendimiento de fósforo en el ensayo I como para el rendimiento total de fósforo ha existido una correlacción altamente significativa con la tasa de CESION que presentan estos suelos.

Las situaciones que se nos han presentado en estos ensayos I y II de invernadero, se dan de hecho en el campo aunque no en forma tan acentuada. Por tanto si pretendemos en un futuro inmediato hacer una evaluación de las exigencias de estos suelos en este nutriente, deberemos tener presente estos factores de fertilidad.

Actualmente en la investigación existe la tendencia de usar isotermas de adsorción que pueden integrar en un solo valor, todos estos factores como la expresión recomendada por Fox y Kamfrath (1970) (48); Khasawneth FE y J.P. Copeland (1973) (95).

Otros investigadores como Ozanne et al 1968 (124); Rajan SS 1973(133), señalan que una concentración dada de fósforo en la solución final, es suficiente para la estimación de las exigencias de un suelo para el rendimiento óptimo de un cultivo.

Ambos criterios nos parecen valiosos para una evaluación de las exigencias de un suelo en fertilización fosfatada.

En estos suelos calizos estudiados que tienen valores próximos de adsorción de fósforo en el lugar I, el aplicar cantidades de fósforo en el rango equivalente (0-1 ppm P en la solución final) nos permitirá tenerlos en condiciones adecuadas para determinar con exactitud a que rango de la concentración de fósforo en la solución final, se obtiene el rendimiento máximo y usando esta expresión de factor de capacidad, se pueda establecer un criterio más adecuado sobre la validez de la estimación que hagan del fósforo asimilable las soluciones extractoras, Olsen y Burriel-Hernando.

Para establecer, las exigencias en este nutriente entre suelos calizos y no calizos, tal vez resulte más efectivo usar la expresión recomen dada por Fox-Kamprath y Khasawneth F.E. y J. P. Copeland, que en un valor incluya todos los factores de fertilidad considerados ya que se puede dar el caso de que se obtenga el máximo rendimiento de un cultivo a concentraciones distintas de fósforo en la solución final.

CHAPTER 6

SUMMARY

RESUME

RESUMEN

CHAPTER 6

SUMMARY

The phosphorus situation of some representative soils (Gypsum serosem, Marly serosem, Terrace soil, Alluvial meadow soil from Gallego River, and Brown soil) of Saragossa province, is studied in this work which involves the total phosphorus distribution along the different soil profile, the physico-chemical soil properties related to phosphorus and the dynamics of this nutrient in the plant growing.

Concerning the total phosphorus distribution, in calcareous soils it was found that its content decreases according to soil depth; being this falling off more pronunced in gypsum serosem and terrace soil (60.2 to 17.8 and 75.3 to 23.3 mg P/100 g soil) than in alluvial meadow soil and marly serosem (70.9 to 41.8 and 28.6 to 21.6 mg P/100 g soil).

Brown soil shows a different distribution to that belonging to the calcareous soils and its characteristic is that the total phosphorus content in Bvcv horizon is similar to that of Ap horizon and higher than that of Bv horizon.

The organic phosphorus contents has a variation along the soil profile in these five soils, which is similar to that pointed out for total phosphorus.

A further and deeper study related to organic phosphorus determination is thought to be necessary since that the distribution of this form followed the same pattern in all soils, there were some differences between the figunes obtained by both procedures.

En calcareous soils, the dominant inorganic phosphorus fraction is the one bound to calcium, while in Brown soil it is the soluble in

reductant. Their contents au reflected through a similar value in all soil horizons.

The soil physico-chemical properties related to phosphorus are deduced through the measure of the adsorption, desorption and the liberation of the phosphorus added to soil.

In this study, the phosphorus adsorption by the arable layer of these five different soils was determined, infering that the K_1 and K_2 values calculated from the Langmuir modified equation, are independent in both, in the phosphorus form added and in the presence or absence of calcium chloride. In calcareous soils it was recommended to use a procedure which includes a medium calcium chloride and a form of P added like calcium diphosphate.

Studing the phosphorus desorption in these soils, through two laboratory procedures, it was found that the behaviour of these soils diverges in relation to the rate and the P ammount liberated. In the case of Gypsum serosem, Maral serosem, and Brown soil, the phosphorus liberation is governed by the solubility of thein P compounds; while in Terrace and Alluvial meadow soil are characterized by a typical desorption process.

If the ratio between adsorption of P added and the ammount liberated by a desorption process subsiguient is considered, the soils such as Gypsum serosem, Marly serosem, and Alluvial meadow soil shown a similar % of P liberated, although their quantities of P adsorbed are different; while in the case of Brown soil and Terrace soil such a percentage becomes higher although the latter has the same quantity of P adsorbed as the oue of the calcareous Soil (Marly serosem). Under greenhouse conditions, the soil phosphorus dynmacis and the P yield of rye-grass is related, so:

In the five soils, the P fraction soluble in ammonium chloride solution contributed significatively to the P yield of rye-grass while in calcareous soils the P-Ca fraction becomes significant.

From three extracting procedure for soil P available, only the van der Paauw-Sissingh method reflects well this soil P absorbed by plant.

The differences in dry matter and P yields are observed in rye-grass grown on these five soils; they are discussed through the fertility soil factors (intensity, quantity, buffering capacity and rate P desorption) which govern the supply of this nutrient to a crop.

CHAPITRE 6

RESUME

Dans ce travail on étudie la situation du phosphore dans les sols - qui sont representés dans la province de Saragosse : Serosem plâtreux, - serosem margueux, brun calcaire sur terrace, vega du fleuve gallego et terre brune; en considérant la distribution du phosphore total, organique et inorganique tout au long des différents horizons; les propriétés physico-chimiques du sol en relation au phosphore et la dynamique du phosphore dans la croissance des plantes.

Quant à la distribution du phosphore total, il se trouve que son - contenu diminu avec la profondeur du profil dans les sols calcaires. Cette diminution est dans les sols serosem plâtreux et brun calcaire sur - terrace plus accousée (60.2 à 17.8 et de 75.3 à 23.3 mg P/100 g de sol) - que dans les sols de vega du fleuve gallego et serosem margueux (70.9 à 41.8 et de 28.6 à 21.6 mg P/100 g soil).

La terre brune présente une distribution différente à celle des sols calcaires et se caractérise parce que le contenu de phosphore total dans l'horizon inférieur (Bvcv) est similaire à celui de l'horizon superficiel (Ap) et supérieur à l'horizon intermédiaire.

Le contenu de phosphore organique souffre une variation tout au - long du profil dans les cinq sols, similaire à celle indiquée par le phosphore total.

On considère nécessaire pour les résultats obtenus d'approfondir dans l' étude de la determination du phosphore organique quoique la distribution continue son cours parallèle il y a des différences dans les valeurs quantitatives de dite forme de phosphore determiné par les deux méthodes.

Dans les sols calcaires, la forme dominante est celle liée au cal-

cium, tandis que dans la terre brune c'est celle qui est soluble en réductant. Le contenu des deux fraction se caractérise par une constance dans tous les horizons.

Les propriétés physico-chimiques du sol en relation au phosphore se déduisent quand on étudie l'adsorption, desorption et libération du phosphore ajouté au sol.

Dans ce travail on détermine l'adsorption du phosphore par la couche labourable des cinq sols différents, en déduisant que les valeurs K_1 (constante de retention) et K_2 (adsorption maximum) calculées au moyen de l'equation modifiée de Langmuir, sont indépendantes dans le cas de la terre brune, tant dans la fome de phosphore ajouté comme de la présence ou absence de chlorure calcique. Dans les sols calcaires on recommande de réaliser ces études avec du phosphate monocalcique et en présence de chlorure calcique.

En étudiant le phosphore par 2 méthodes de laboratoire, on trouve que le comportement des sols diffère en ce qui respete à la quantité d'élément libéré comme à la rapidité de cette libération. Dans le cas de sols Serosem plâtreux, serosem margueux et terre brune, la libération du phosphore est régulée par la solubilité de ses composés tandis que dans les sols brun calcaire sur terrace et vega du fleuve gallego on indique un procès typique de désorption.

Si on considère la relation entre adsorption du phosphore ajouté avec la quantité d'élément qui se libère par un procès de desorption subsuivant, les sols serosem plâtreux, serosem margueux et vega du fleuve gallego présentent un pourcentage similaire de libération quoique les quantités adsorbée diffèrent légèrement; tandis que dans les sols terre brune et brun calcaire sur terrace, ce pourcentage est supérieur quoique ce dernier sol présente une quantité de phosphore adsorbé similaire à celle d'un des sols calcaires (serosem margueux).

Sous les conditions de serre, on considère la dynamique du phosphore du sol et le rendement du phosphore de l'avoine fourragère obtenu, ainsi:

Des fractions de phosphore inorganique, la soluble en chlorure d'ammonium dans les cinq sols contribua significativement au rendement de phosphore de cette culture et dans le cas des sols calcaires la fraction de P soluble en acide sulphurique tend à être significative.

Des trois procès d'extraction de phosphore assimilable étudiés, seul celui de Van der Paawn-Sissingh reflete bien le phosphore du sol absorbé par la plante.

Les différences qui s'observent en rendement de matière sèche et en phosphore de l'avoine fourragère grandit dans ces cinq sols, on discute en fonction des facteurs (intensité, quantité, capacité et taux de cession) qui régulent l'aprovisionement de ce nutriment à une culture.

CAPITULO 6

RESUMEN

En este trabajo se estudia la situación del fósforo en los suelos representativos de la provincia de Zaragoza. Serosem Yesoso, Serosem Margoso, hardo calizo sobre terraza, vega del río Gállego y tierra parda; considerando la distrubución del fósforo total, orgánico e inórgánico a lo largo de los distintos horizontes; las propiedades físico químicas del suelo en relación al fósforo y la dinámica del fósforo en el crecimiento de las plantas.

Por lo que respecta a la distribución del fósforo total, se encuentra que su contenido disminuye con la profundidad del perfil en los suelos calizos. Esta disminución es en los suelos Serosem Yesoso y pardo calizo sobre terraza más acusada (60,2 a 17,8 y de 75, 3 a 23,3 mg P/100 g de suelo) que en los suelos vega del río Gállego y Serosem Margoso (70,9 a 41,8 y de 28,6 a 21,6 mg P/100 g suelo).

La tierra parda presenta una distribución distinta a la de los suelos calizos y se caracteriza porque el contenido del fósforo total en el horizonte inferior (BVCV) es similar al del horizonte superficial (AP) y superior al horizonte intermedio.

El contenido del fósforo orgánico sufre una variación a lo largo del perfil en los cinco suelos, similar a la señalada para el FOSFORO TOTAL.

Se considera necesario por los resultados obtenidos, profundizar en el estudio de la determinación del fósforo orgánico aunque la distribución sique un curso paralelo hay diferemcias en los valores cuantitativos de dicha forma de fosfóro determinado por dos de los métodos.

En los suelos calizos, la forma dominante es la ligada al calcio mientras que en la tierra parda es la soluble en reduntante. El conte nido de ambas fracciones se caracteriza por una constancia en todos los horizontes.

Las propiedades físico-químicas del suelo en relación al fósforo se deducen al estudiar la adsorción, desorción y la liberación del fósforo añadido al suelo.

En este trabajo se determina la adsorción de fósforo por la capa arable de los cinco suelos distintos, deduciéndose que los valores K1 (constante de retención), y K2 (adsorción máxima) calculados mediante la ecuación modificada de Langmuir, son independientes en el caso de la tierra parda tanto en la forma de fosfóro añadido como de la presencia o ausencia de cloruro cálcico. En los suelos calizos se recomienda realizar estos estudios con fosfato monocálcico y en presencia de cloruro cálcico.

Se estudia la desorción de fósfòro por dos métodos de laboratorio, se encuentra que el comportamiento de los suelos difiere en lo que respecta a la cantidad de elemento liberado como a la velocidad de esta liberación. En el caso de los suelos Serosem Yesoso, Serosem Margoso y tierra parda, la liberación del fósforo está regulada por la solubilidad de sus compuestos mientras que en los suelos pardo calizo sobre terraza y vega del río Gállego señala un proceso típico de desorción.

Si se considera la relación entre adsorción de fósforo añadido con la cantidad de elemento que se libera por un proceso de desorción subsiguiente, los suelos Serosem Yesoso, Serosem Margoso y vega del río Gállego presentan un % similar de liberación a pesar de que las cantidades adsorbidas difieran ligeramente; mientras que en los suelos tierra parda y pardo calizo sobre terraza, dicho porcentaje es superior aunque este último suelo presente una cantidad del fósforo adsorbido similar a la de uno de los suelos calizos (Serosem Margoso).

Bajo condiciones de invernadero, se considera la dinámica del fósforo del suelo y el rendimiento del fósforo del centeno forrajero obtenido, así:

De las fracciones de fósforo inorgánico, la soluble en cloruro de amonío en los cinco suelos contribuyo significativamente al rendimiento de - Fósforo de este cultivo, y en el caso de los suelos calizos la fracción de P soluble en ácido sulfúrico tiende a ser significativa.

De tres procedimientos de extracción de fósforo asimilable estudiados, solo el de Van der Paauw Sissingle refleja bien el fósforo del suelo absorbido por la planta.

Las diferencia que se observan de rendimiento en materia seca y en fósforo del centeno forrajero crecido en estos cinco suelos, se discuten en función de los factores (intensidad, cantidad, capacidad y tasa de CESION) que regulan el suministro de este nutriente a un cultivo.

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