

Gradient elution of soil columns

Gradient eluering af jordsøjler

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Summary

In this paper the results are shown from experiments where soil columns were eluated with an acid gradient. The gradient was made by electronic directions from a so-called ultrograd.

P, K, Cu and Zn were determined in the eluates from the columns. It was shown that the concentration curves of eluates were characteristic of each soil type and element. Also the solubility of some P-compounds generally present in soils were studied by gradient elution. Probably this technique can be used for investigations of the solubility of several elements and chemical compounds in soil.

Key words: Gradient elution, plant nutrients, soil.

Resumé

Ved jordbundskemiske undersøgelser er der ofte behov for at opdele et plantenæringsstof i fraktioner efter deres opløselighed og tilgængelighed for planterne. Der er i beretningen peget på forskellige muligheder for en sådan adskillelse f.eks. ved ekstraktion med forskellige opløsninger samt ved placering af jordprøven i et elektrisk felt, hvorved anioner går til anoden og kationer til katoden.

Ved denne undersøgelse anvendtes gradienteluering til undersøgelse af opløseligheden i jord af forskellige P-forbindelser samt K, Cu og Zn. Gradienten blev fremstillet af en såkaldt ultrograd, og eluatfraktioner af 40 ml blev opsamlet i 24 glas. Ved elueringen kan flere parametre varieres f.eks. opløsningerne i de 2 reservoirs, styrekurven i ultrograden, elueringshastigheden og søjletemperaturen. Ved denne undersøgelse blev jordsøjlerne elueret med en pH-gradient fra 7,0 til 1,0 og en hastighed af 2 ml pr. min.

Som ventet var pH i eluatfraktionerne forskellig for jordene, og det fremgik af diagrammerne, at plantenæringsstoffernes opløselighedskurver er stærkt afhængige af jordenes kalkindhold. Der fandtes ved elueringen 2 eller 3 toppe i diagrammet for hvert af de undersøgte plantenæringsstoffer, og et højt Cu-indhold i en af prøverne kunne henføres til, at denne jord tidligere var behandlet med Cu-holdige sprøjtemidler.

Det kunne påvises, at forskellige tilsatte P-forbindelser blev elueret fra jordene i rækkefølgen KH_2PO_4 , Ca-phosphat (Casa-råphosphat) samt AlPO_4 og FePO_4 , og i de ubehandlede jorde fandtes toppe for hver af de ovennævnte P-forbindelser. I rent sand blev KH_2PO_4 elueret kvantitativt med vand, medens Ca-phosphat blev genfundet kvantitativt ved eluering med HCl-opløsning – pH ca. 3,0. AlPO_4 og FePO_4 tilsat sand blev med den anvendte gradient kun i ringe grad genfundet. Undersøgelserne viste, at uorganisk P i de undersøgte jorde groft kan grupperes som letopløselige P-forbindelser, Ca-phosphater og Al- og Fe-phosphater.

Den elueringsteknik, som er beskrevet i denne beretning, kan sandsynligvis anvendes til de fleste grundstoffer og kemiske forbindelser. Ved at variere de angivne parametre for gradienteluering i henhold til grundstof, kemisk forbindelse og jordtype kan adskillelsen i toppe optimeres. Organiske forbindelser i jorden kan muligvis også adskilles på denne måde f.eks. ved at anvende organiske opløsningsmidler til eluering af organiske P-forbindelser fra jordsøjler.

Nøgleord: Gradienteluering, plantenæringsstoffer, jord.

Introduction

The degree of solubility of different plant nutrients in soil varies. Also within the same elements solubility can vary from slightly soluble to exchangeable or water soluble fractions. K and P are examples of this and the greater part of these two elements are present in soil as poorly soluble compounds almost non-available to plants.

In soil chemistry attempts are being made to separate plant nutrients into fractions according to their availability to plants, e.g. water-soluble, exchangeable and acid-soluble. This is done for most plant nutrients. The division is frequently made on the basis of a chemical extraction. The most soluble part of soil-P can be determined by e.g. extraction with H_2O (Paauw, 1971); NaHCO_3 (Olsen *et al.*, 1954); anion-buffer-resin (Amer *et al.*, 1955) or equilibration with ^{32}P (Ruszel *et al.*, 1954; Larsen, 1952). The most plant available part of P and K in the soil can be extracted with ammonium-lactate-solution (Egnér *et al.*, 1960) and the acid soluble part can be dissolved with boiling 2 N HCl (Ståhlberg, 1976). For the majority of essential plant micro nutrients extraction methods are used which approximately evaluate the ability of the soil to supply the plants with the relevant nutrients. Analytical indexes are used for evaluation of soil fertility and figures for the water soluble part, the exchangeable part and the acid soluble part can be used. Sometimes the 3 indexes are used in combination.

Extraction of soil samples placed in an electrical field with varying voltage between the poles is used by Nemeth (1972). This method can be used for estimation of various plant nutrients.

Gradient elution has been used, for example, for investigation of the solubility of soil-P. The gradient can be produced with a system of containers connected in series (Dissing Nielsen, 1975; Olsen & Larsen, 1979).

The object of this investigation was to show that the gradient elution system described in this paper can be an useful aid for soil research. This system was used for elution of soil columns with an acid gradient and P, K, Cu and Zn were determined in the fractions. The same method was also used for investigating the solubility in soil of various inorganic P-compounds usually present.

Apparatus and materials

Apparatus

A diagram is shown in Fig. 1. Two reservoirs containing water and 0.1 N HCl respectively are connected to a magnetic valve electronically regulated from a so-called ultrograd (LKB). The delivery from the two containers is regulated from the curve in the ultrograd. The curve is prepared simply from thick paper (supplied by the firm). A peristaltic pump and a mixing chamber are placed between the magnetic valve and the column. The glass-column is 25 cm high, and its inner diameter is 0.7 cm. A glassfilter G_3 is placed

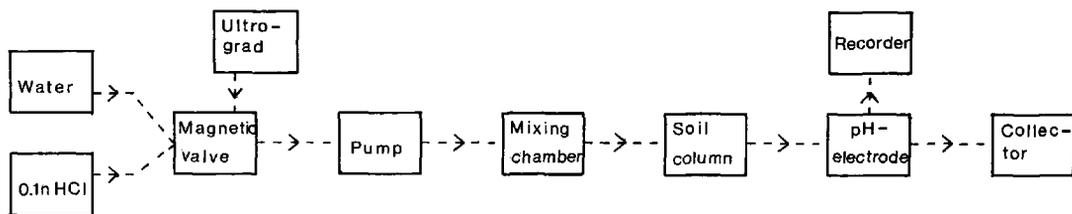


Fig. 1. Diagram of the arrangement of apparatus used for gradient elution.

in the column. The column is filled with 5 g of soil mixed with 10 g of pure sand. The eluate fractions are collected with a fraction-collector and each glass contains 40 ml. A pH electrode connected to a recorder is placed between column and collector.

Parameters

Solvents for elution: H₂O, 0.1 N HCl

Elution speed: 2 ml/min

Gradient curve: Fig. 2

Temperature: room-temperature ca. 20°C

Elution time: 8 hours

The five parameters may be altered for different analytical purposes, and it is also possible to connect more than two containers to the magnetic valve.

Soil

In the experiments three soils and pure sand were used. The soils were taken from the surface layer 0–25 cm, and Table 1 shows some data of the soils.

P-compounds

KH₂PO₄ (Merck)

FePO₄ (Merck)

Casa raw phosphate (Morocco)

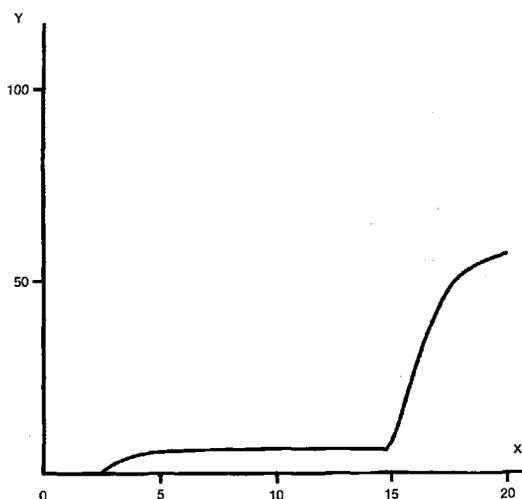


Fig. 2. Curve for regulation of magnetic valve.
y = time in % of time open to 0.1 M HCl bottle.
x = glass no.

Table 1. Some characteristics for the soils used in the experiments

No.	Classification	pH _{H₂O}	Texture per cent				
			Clay	Silt	Fine sand	Coarse sand	Humic
9a	Sandy-clay-soil	6.1	12.8	16.0	41.1	28.4	1.7
33a	Sandy-soil	6.0	2.8	4.7	75.1	15.3	2.1
53a	Organic-soil	7.7	6.9	19.9	38.9	24.1	10.2
	Sand	6.6	0	0		100	0

Analytical methods used for determination of elements

P: photometry

K: flameemission

Cu and Zn: atomic absorption

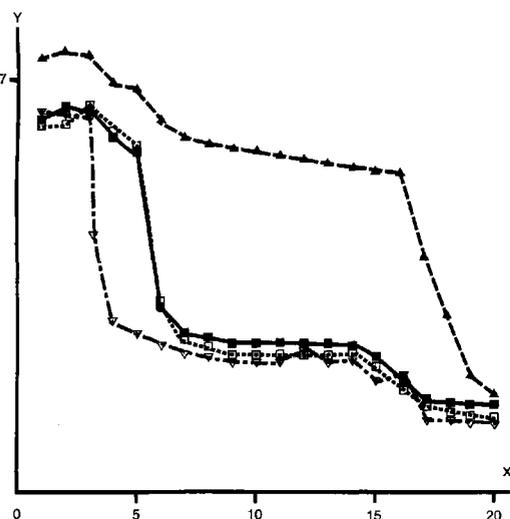


Fig. 3. Curves for pH in eluates from four soils.

y = pH. x = glass no. □ . . . □ 9a; ■ — ■ 33a; ▲ — — ▲ 53a; △ - - - △; sand.

Results

In Fig. 3 the ordinate shows pH of fractions from soil columns and the abscissa glass no. from 1 to 22. For soil 9a, 33a and pure sand pH decreases from about 7 for glass no. 1 to about 1 for glass no. 22. The curves are almost identical for 9a, 33a, and sand but the decrease of pH appears first for eluate fractions from sand. Soil 53a has a higher

buffer capacity because of its content of CaCO_3 and it is neutralized only after glass no. 15 where pH decreases to the same level as for the other soils.

The concentration of elements in eluate fractions collected from soil columns is shown in Fig. 4-6. The curves for 9a and 33a (Fig. 4 and 5) are very much alike for each of the elements. Moreover the peaks are found in the same place for the two soils and also the peaks for the 4 nutrients are found at about the same place in the figures. The concentration of elements in the fractions differs for the two soils. This is mainly true for K and Cu and for these two elements the content in glass no. 5 and 6 is about 3 times higher for soil 9a compared with 33a. As to the lime containing soil (53a) only after glass no. 16 is pH decreased below 3. Until glasses no. 14-15 the fractions from 53a contain some P and K but only small amounts of Cu and Zn. After glass no. 15 there is a peak for both P, K, Cu and Zn.

Table 2 shows the sum of the eluated plant nutrients and, for comparison the amount of the nutrients which are found by the methods used in Denmark for soil testing. Apart from P, the elution method extracted more plant nutrients than soil tests.

In the next experiments elution with an acid-gradient was used for identification and separation of soil P in some main groups. Fig. 7-9 show results from experiments with two soils and sand which were added 20 mg P/100 g soil as various P-compounds generally present in the soil. In Fig. 7 at least three peaks can be seen for soil 9a without added P-compounds. Until

Table 2. Comparison of the eluated quantity and soil fertility-figures for four plant-nutrients. For estimation of soil-figures the following extractions were used: P, 0.2 N H_2SO_4 ; K, 0.5 M NH_4 -acetate; Cu and Zn, 0.02 M EDTA

No.	P		K		Cu		Zn	
	Eluated	Figure mg/100 g soil	Eluated	Figure	Eluated	Figure mg/kg soil	Eluated	Figure
9a	13.2	22.2	31.6	16.0	33.6	27.3	9.2	1.6
33a	17.6	33.2	6.8	5.2	14.5	6.8	12.5	2.2
53a	32.7	41.4	22.3	9.6	13.7	7.8	21.6	6.1

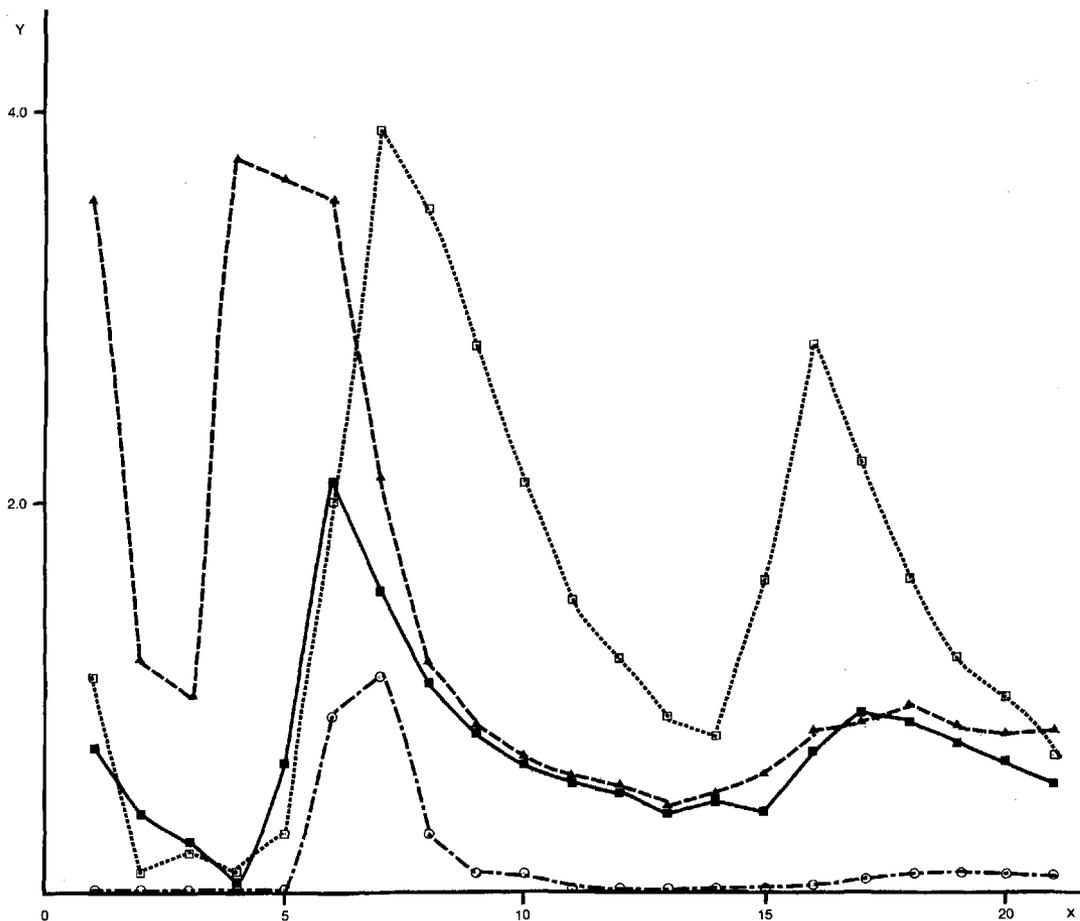


Fig. 4. Curves for content of P, K, Cu and Zn in eluates from soil 9a. $y = \blacksquare\text{---}\blacksquare$ mg P/100 g soil; $\blacktriangle\text{---}\blacktriangle$ mg K/100 g soil; $\square\text{...}\square$ mg Cu/kg soil; $\circ\text{-.-}\circ$ mg Zn/kg soil; $x =$ glass no.

glass no. 5 the solvent is water and only the most soluble part of soil-P is dissolved. A peak appears after glass no. 5 and after glass no. 14–15. A water soluble P-compound, KH_2PO_4 , added to the soil is recovered mainly in the first glasses but addition of KH_2PO_4 to soil 9a has also given a small increase of the P-content in the next glasses. If a raw phosphate, Casa-P, is added to 9a, P is recovered from glass no. 5 until glasses no. 14–15. That corresponds approximately with the second peak for 9a without added P. Furthermore Fig. 7 shows results from an experiment with addition

of FePO_4 to the soil and it is seen that this compound mainly has an effect on P-content after glass no. 15.

In Fig. 8 analogous results are shown for a sandy soil 33a. The peaks for P-content after elution of 33a without added P appear at the same place as for 9a. Added KH_2PO_4 to the soils appears earlier in the diagram for 33a compared with 9a, and Casa-P appears in the same glasses for the two soils. Added KH_2PO_4 -P to sand (Fig. 9) is almost recovered in glasses no. 1–2 and Casa-P added to sand is recovered in glasses no. 5–14.

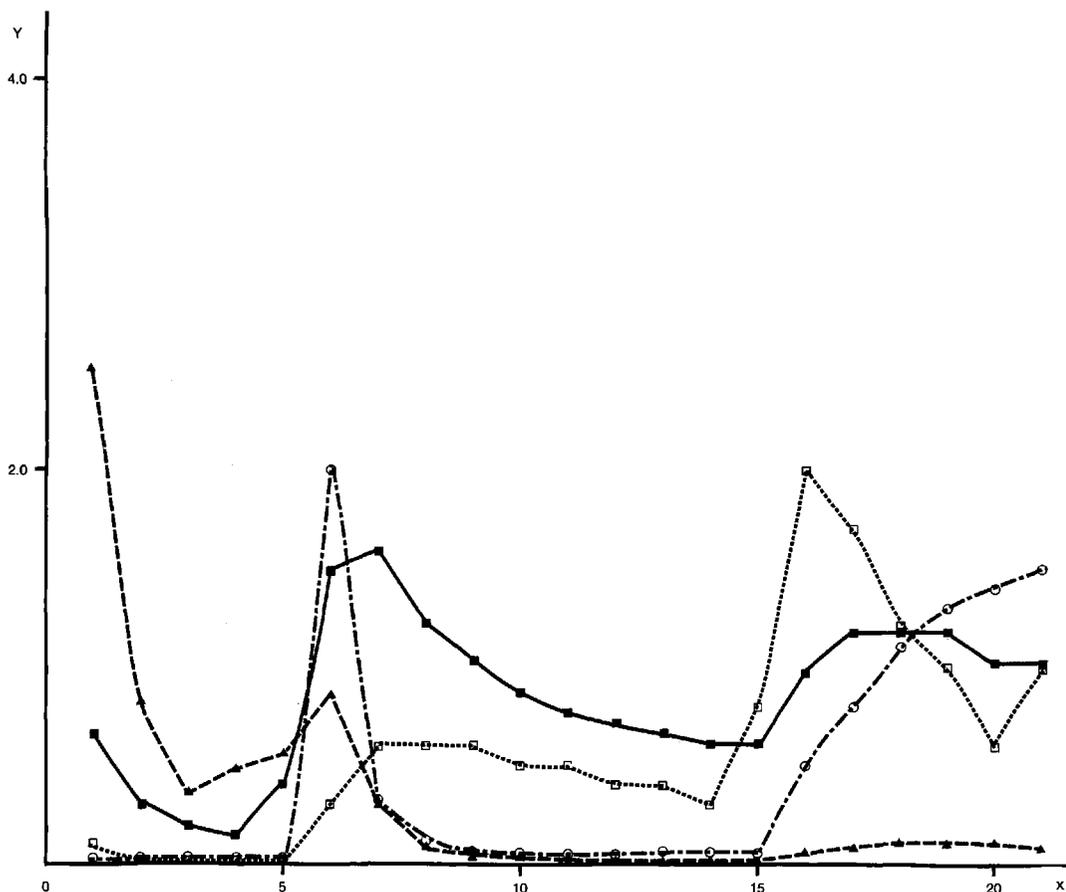


Fig. 5. Curves for content of P, K, Cu and Zn in eluates from soil 33a. Marked as for Fig. 4.

$\text{FePO}_4\text{-P}$ appears after glass no. 14 but only a small part of the added $\text{FePO}_4\text{-P}$ is recovered.

Table 3 shows the sum of inorganic P eluated from the soil column. The added P in KH_2PO_4 and Casa is fully recovered for sand and to a great extent also for the two soils. The majority of added $\text{FePO}_4\text{-P}$ is not dissolved during the elution process, but in the last part of the elution FePO_4 is partly soluble. Analogous results were found for AlPO_4 .

Discussion and conclusion

For elution of soil columns an acid gradient was used in these experiments and P, K, Cu and Zn

were estimated in the eluates. These four elements were elected due to the fact that they are common in soils. They are known also to be essential for plant growth and P and K in particular are applied to the soil e.g. in fertilizers.

The regulating curve shown in Fig. 2 was found in several preliminary experiments to be well suited for this investigation. By using a regulating curve giving a lesser pH-decrease the elution pattern can differ more for soils and elements but in this investigation it was preferred to use the same procedure for various soil types and elements. The pH-curves of the eluates were not linear and it depends on the type of the eluated

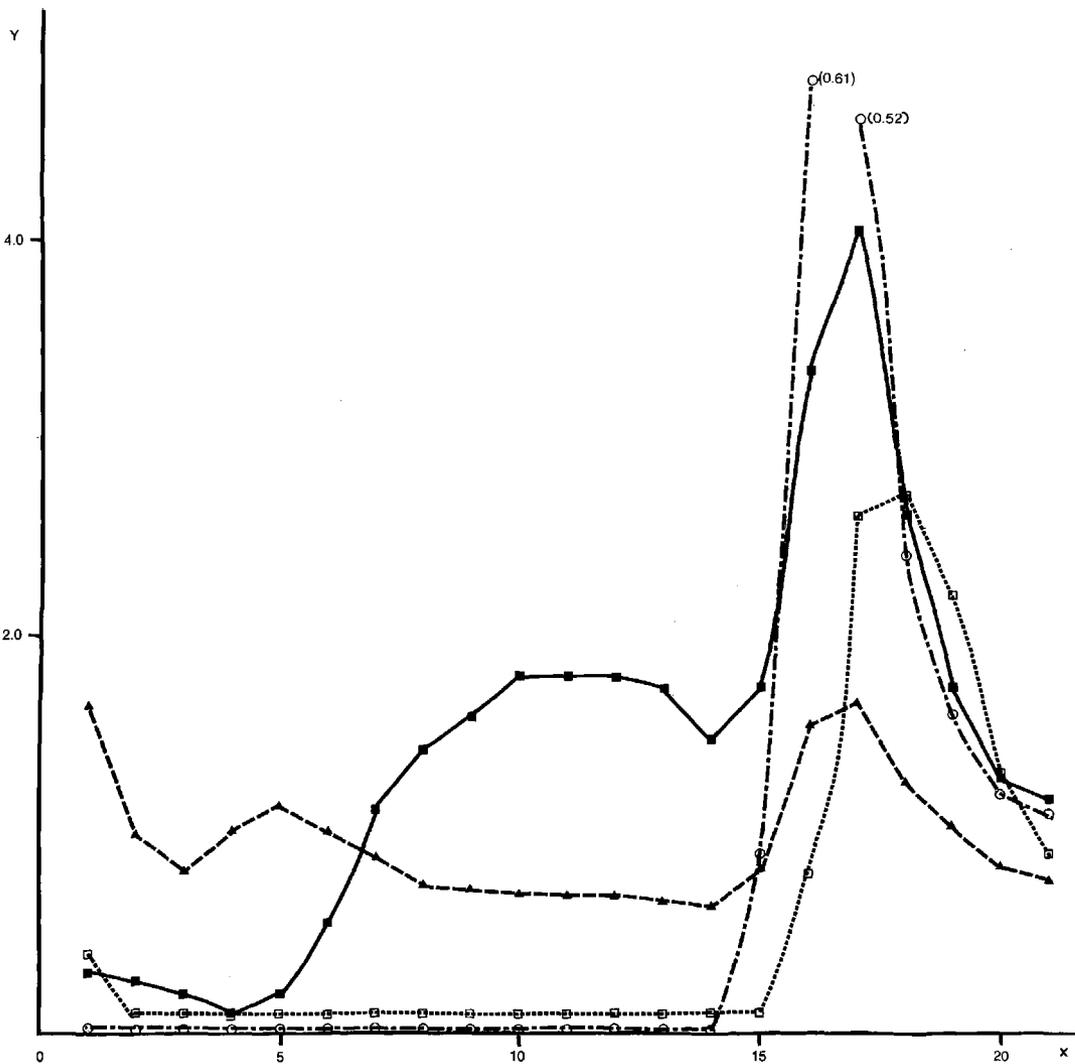


Fig. 6. Curves for content of P, K, Cu and Zn in eluates from soil 53a. Marked as for Fig. 4.

soil. For all four eluated elements there was a clear connection between solubility and pH of eluates. This was also found for the P-compounds added to soils.

The elution diagram can be used for evaluation of plant availability and risk of leaching of elements. Its most soluble part will be released during the first part of the elution. E.g. 9a has a high

Cu-figure (Table 2) and it was mainly found in glasses no. 5 to 10 (Fig. 4). In this soil relatively more Cu was easily soluble than for soil 33a with normal Cu-figure. The large amount of Cu extracted from 9a is probably due to the fact that Cu-containing chemicals had been used for this orchardsoil. Also for P it was shown (Dissing Nielsen, 1975) that it is relatively more soluble in

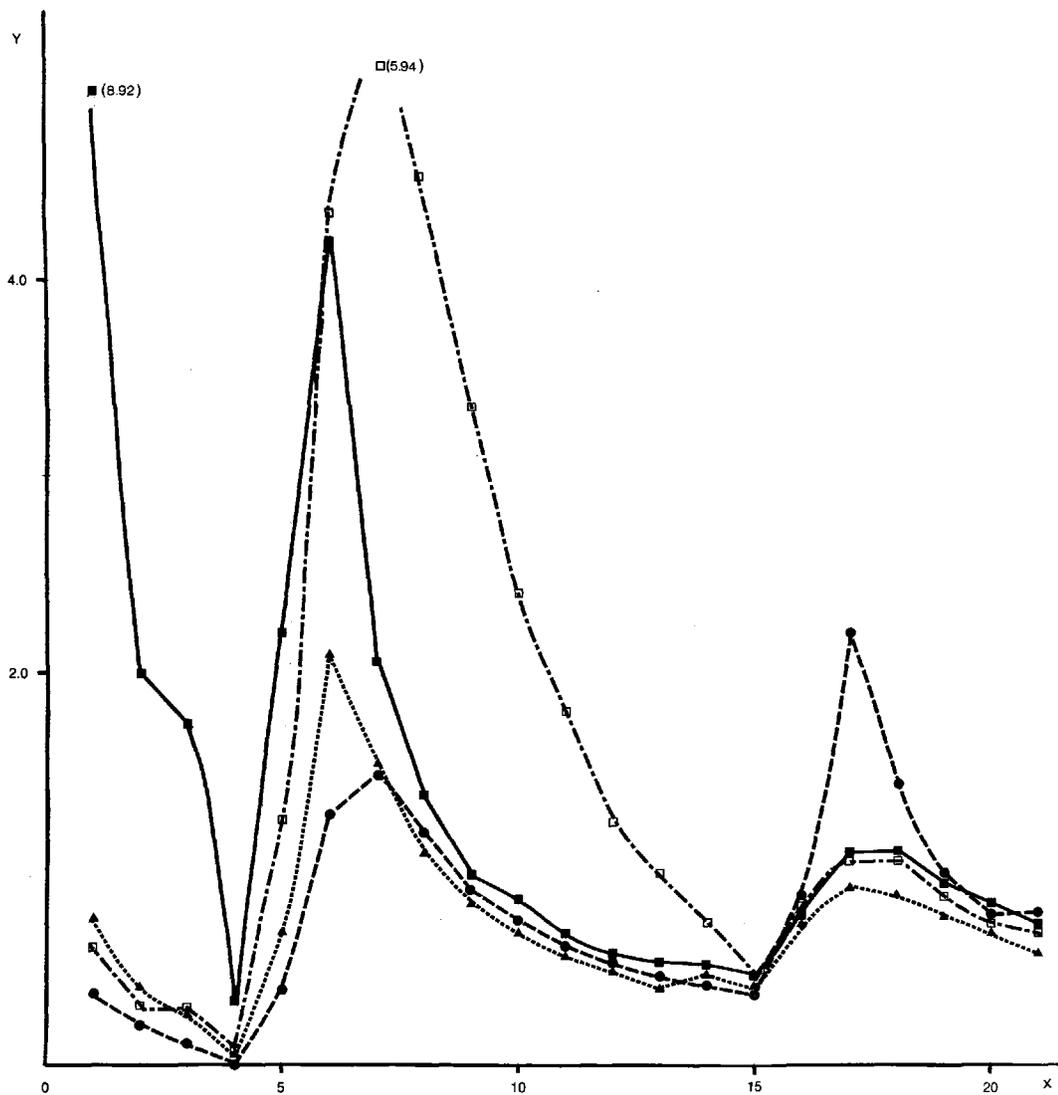


Fig. 7. Curves for content of P in eluates from soil 9a with various P-compounds added. $y = \text{mg P}/100 \text{ g soil}$; $\blacktriangle \dots \blacktriangle$ soil only; $\blacksquare \text{---} \blacksquare$ soil + KH_2PO_4 ; $\bullet \text{---} \bullet$ soil + FePO_4 ; $\square \text{---} \square$ soil + Casa-P. $x = \text{glass no.}$ Some values for Fig. 7, 8 and 9 are outside the diagram. The content in these glasses are given in the brackets.

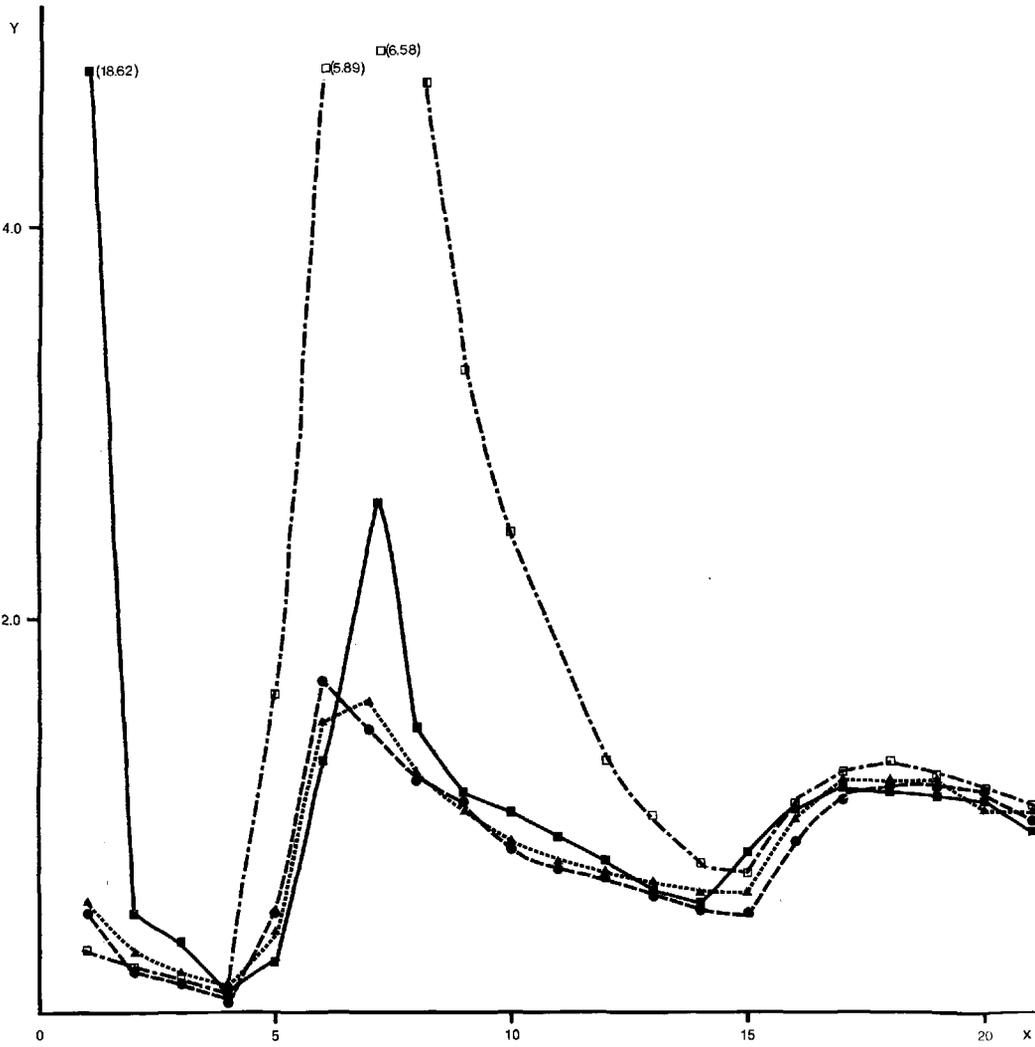


Fig. 8. Curves for content of P in eluates from soil 33a with various P-compounds added. $y = \text{mg P}/100 \text{ g soil}$.
Marked as for Fig. 7. $x = \text{glass no.}$

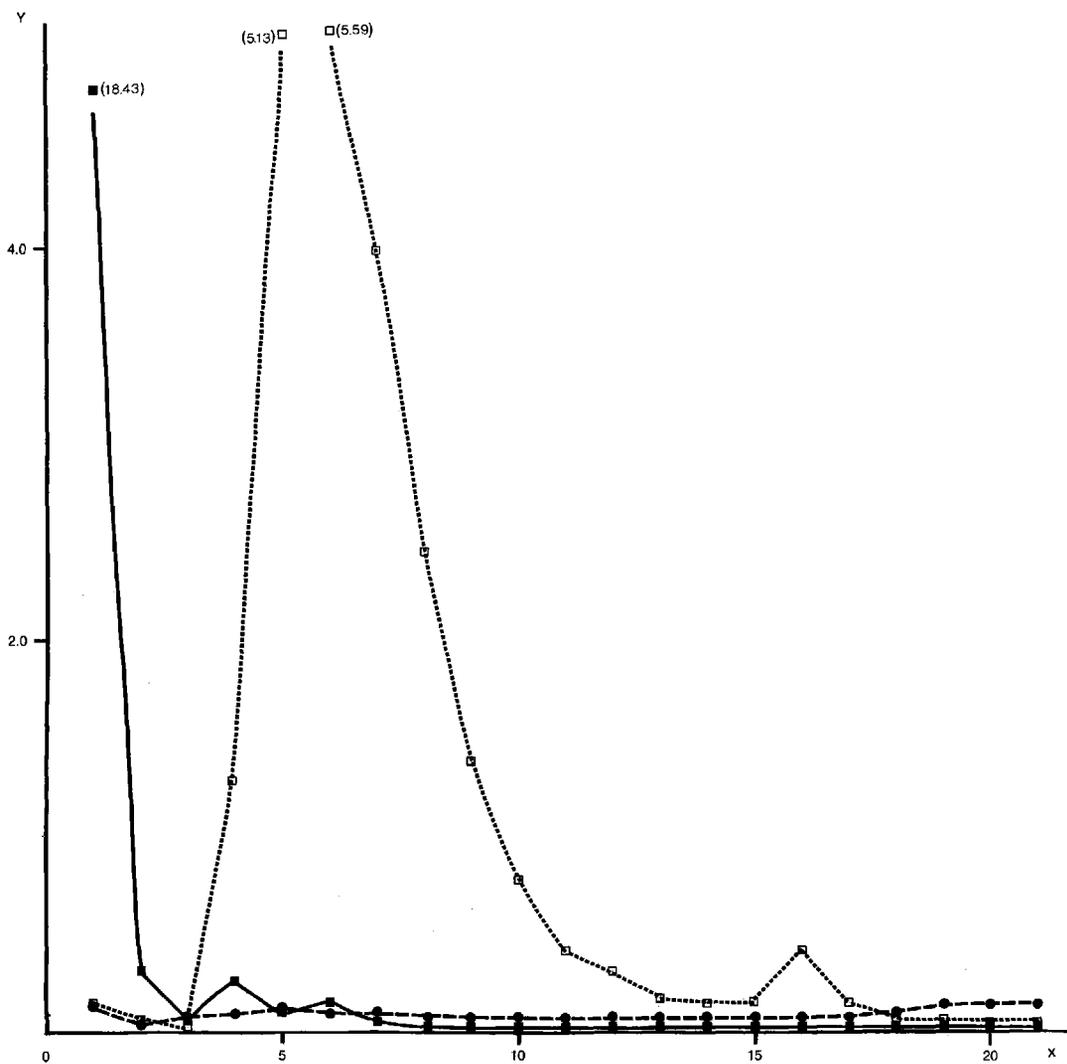


Fig. 9. Curves for content of P in eluates from sand with various P-compounds added. y = mg P/100 g sand. Marked as for Fig. 7. x = glass no.

Table 3. Elution of P from 2 soils and sand with various P-compounds added

	mg P/100 g soil in glass No.			
	1-4	5-14	15-22	1-22
9a	1.47	8.82	5.43	15.72
9a + 20 mg KH ₂ PO ₄ -P/100 g soil	12.97	13.83	6.41	33.21
9a + 20 mg Casa-P/100 g soil	1.23	25.84	6.29	33.36
9a + 20 mg FePO ₄ -P/100 g soil	0.66	7.78	7.93	16.37
33a	1.21	9.37	8.08	18.66
33a + 20 mg KH ₂ PO ₄ -P/100 g soil	19.59	10.59	8.06	38.24
33a + 20 mg Casa-P/100 g soil	0.77	29.47	8.46	38.70
33a + 20 mg FePO ₄ -P/100 g soil	0.91	9.47	7.64	18.02
20 mg KH ₂ PO ₄ -P/100 g sand	19.00	0.30	—	19.30
20 mg Casa-P/100 g sand	1.53	20.32	0.76	22.61
20 mg FePO ₄ -P/100 g sand	—	0.47	0.90	1.37

soils fertilized with P than in soils with no P-application. Compared to the quantity figures used for evaluation of soil fertility the elution method can give some qualitative evaluation of the solubility of plant nutrients.

The soil test method extracted more P than was found by the gradient elution, probably because the former include almost all the inorganic P. For the other nutrients more was extracted by the gradient elution than by the soil test methods, possible due to the acidity of the elution solvent. This acidity could have released some non-exchangeable K from the clay fraction.

Some P-compounds were added to three soil types: sandy-clay soil, sandy soil and pure sand. The results from those experiments showed that the added P appears in the same place in the diagram for the two investigated soils and sand. Analogous peaks were found in the diagrams for soils with and without addition of various P-compounds. After mixing of KH₂PO₄ or Casa-P with soil or sand the added P was recovered nearly quantitatively in the eluates. P from easily soluble compounds may react in the column with soil particles and in this way the solubility of P can be decreased and thereby delayed. For soil 9a addition of FePO₄ reduced the P-content in glass no. 5 and 6 probably as a result of formation of insoluble P-Fe-compounds.

The experiments showed for the investigated soils that inorganic P can be grouped roughly as: 1. easily soluble P-compounds e.g. KH₂PO₄; 2. Ca-phosphates like Ca-phosphates in various raw-phosphates and 3. Fe- and/or Al-phosphates.

The order of elution of P-compounds found in these experiments can differ from the order of plant availability which depends on soil type and soil-pH. According to *Kick and Minhas (1972)*, *Ivanow and Sauerbeck (1972)*, and *Dissing Nielsen (1975)*, in acid and neutral soils inorganic P is mainly present in the form of Al- and Fe-phosphates and in alkaline soils it is predominantly found as Ca-phosphates.

The elution technique described in this paper can probably be used for the majority of elements, and by variation of the stated parameters for gradient elution it may be possible to increase the separation of an element. Possibly some organic compounds in the soil may also be separated in this way e.g. P-containing organic compounds by using organic solvents.

As mentioned before the technique used in these investigations is very flexible. This is an advantage for the use of gradient elution of soil columns. In this experiment the technique has been used for fractionation of P, K, Cu and Zn in soil and to identify main groups of P-compounds in soil. Gradient elution can probably also be used

for various soil investigations e.g. for estimation of the content and the solubility of heavy metals following large amounts of waste products and chemicals. Probably more research on the use of this method for individual soils and elements can increase its value.

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