

Phosphate solubility in three types of light soil in different acids and at different pH (a contribution to Mitscherlich's Gemeinschaftsarbeit)

(Solubilité de l'acide phosphorique dans trois types de sol léger dans des acides différents et à un pH variable. [Une Contribution au travail en coopération de Mitscherlich]. — Phosphatlöslichkeit in verschiedenen Säuren und bei verschiedenem pH in drei verschiedenen Typen leichten Bodens. [Ein Beitrag zu Mitscherlich's Gemeinschaftsarbeit])

by

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The Report of the round the table conference, held in Königsberg in 1936¹⁾, during which the results were discussed of comparative testing of soil samples in a number of institutes, contains — amongst other items of great interest to all workers on soil fertility problems — an incitement²⁾ to study the different methods of phosphate determination by acids more closely by

- a) comparing phosphate solubility more systematically at different pH and for different acids;
- b) determining the other substances, brought into solution by those different acids, and their possible influence on phosphate solubility.

¹⁾ Erster Bericht über die Arbeiten und über die Tagung der Arbeitsgemeinschaft zur Prüfung der Laboratoriumsmethoden für die Bestimmung des Kali- und Phosphorsäurebedürfnisses der Böden, Königsberg 12—19 Juli 1936. Obtainable from Dr. D. J. Hissink, Groningen, fl. 4.—

²⁾ l. c. page 90 point 4.

As a contribution to this topic from our side, we discuss in the following the results obtained by three acids — citric, lactic and hydrochloric — on three types of light soil, for which we have taken a moorkolonial soil³⁾, a heath reclamation soil⁴⁾ and an iron containing sandy soil⁵⁾, three types in which we studied the phosphate regime in detail during several years, partly on experimental fields with increasing amounts of phosphate, and partly in pots.

Description of the three types of soil

The three types of soil, used for this comparative study, have been described in the publications referred to above; for the benefit of the present reader we bring together the principal data in Table I, in which the terms have the following meaning:

humus: the loss on ignition of the soil after air drying, sieving through a 1 mm sieve, and drying at 105° C; calculated as % on the soil dried at 105° C.

pH: pH in water (1 : 5) after 24 hours standing at 25° C and reading electrometrically according to the chinhydron method (reading within 1/2 minute after addition of the chinhydron).

Sand and clay: soil treated according to International Method A; separation of fractions according to the Kopecky method (upper limit for clay fraction 0.015 mm).

P-number: mg P₂O₅ per 100 g soil, dissolved by CO₂-containing distilled water at 50° C (1 : 10), description see ⁶⁾.

P-citr: mg P₂O₅ per 100 g soil, dissolved by 1% citric acid, description see ⁶⁾.

P-total: according to the Lemmermann method (aqua regia).

P-fixation: determined by adding Ca (H₂PO₄)₂ solution, description see ⁶⁾.

P-unit: indicates the number of kg of (added) P₂O₅ corresponding with one unit in P-number or P-citr. This figure, of course,

³⁾ O. de Vries und C. W. G. Hetterschij: Der Phosphorsäure-Haushalt in moorkolonialem Boden. Die Phosphorsäure 5, 46 (1935).

⁴⁾ O. de Vries und C. W. G. Hetterschij: Der Phosphorsäure-Haushalt im Heidesandboden (1935). Copies obtainable at the Rijkslandbouwproefstation, Groningen.

⁵⁾ O. de Vries und C. W. G. Hetterschij: Fosfaathuishouding in een ijzerhoudenden zandgrond (mit deutscher Zusammenfassung). Verslagen van Landbouwkundige Onderzoekingen 43, 171 (1937); the Hague, Landsdrukkerij.

⁶⁾ O. de Vries und C. W. G. Hetterschij: Der Phosphorsäure-Haushalt in moorkolonialem Boden, Die Phosphorsäure 5, 40 (1935).

depends upon the thickness of the surface layer and its weight per unit of volume.

Fe: dissolved by boiling the soil for one hour with 25% hydrochloric acid.

Table I

Principal data about the three types of soil
Wichtigste Daten für die drei Bodentypen (Versuchsfeld Pr 87 auf moorkolonialem Boden; Pr 113 auf neu urbar gemachtem Heidesand; Heino, eisenhaltiger Sandboden)

	Pr 87 moor- colonial	Pr 113 sandy	Heino, iron containing sand
Humus %	3.8	3.0	6.9
pH	5.2	4.6	5.7
pH of limed plot	—	5.5	—
Sand > 0.015 mm %	94.7	93.5	82.6
Coarse sand > 0.09 mm %	70.7	76.0	64.2
Fine sand 0.09—0.015 mm %	24.0	17.5	18.4
clay < 0.015 mm %	1.5	3.5	10.5
P-number, mg P ₂ O ₅ /100 g	2 ¹ / ₂	0	0
P-citr, " " } of plots {	10	7	10
P-total, " " } without {	18	18	120
P-fixation % } phosphate {	18	98	88
P-unit, kg/ha P ₂ O ₅	15	15	15
Thickness of upper layer, cm	12	10	12 ¹ / ₂
Weight per volume	1.25	1.5	1.2
Fe %	0.12	0.14	2.2

Note. The plot on experimental field Pr. 87, from which soil was taken for this investigation, had been limed in 1929; the Heino soil had probably been limed several years ago.

The original Heino soil, before sieving, contained pieces of bog ore; the amount of Fe was 6½%.

A preliminary survey of phosphate solubility in water, citric acid and aqua regia for these three soils was given in a paper⁷⁾, in which we compared the "total" phosphate content according to the Lemmermann method (aqua regia) with the phosphate in 1% citric acid (P-citr) and the phosphate in distilled water containing the ordinary amount of carbonic acid (P-number), both after our usual routine methods. For this comparison, the values, obtained according to these three methods, were plotted against pH; the curves, obtained in that way

⁷⁾ O. de Vries, C. W. G. Hetterschij und F. v. d. Paauw, Zeitschr. Bodenk. u. Pflanzenern. 6 (51), 144 (1938).

and depicted in figs 5—7 of the above named publication, give a certain insight into phosphate solubility and phosphate availability in those three types of soil; but they should be regarded, as was already pointed out, with a certain reserve, because they bring into relation the figures obtained by three heterogeneous methods, as we use them in our routine research and soil testing work. These curves do not represent phosphate solubility curves in the strict sense of the word; a solubility curve, of course, relates to one acid only. The curves, as given in the above named publication, served to give a preliminary insight into the phosphate problem for these soils; they do not represent systematic data on a scientific basis. Aqua regia, citric acid and water have different dissolving power for the different soil constituents; the amount of phosphate, brought into solution at a certain pH, may be influenced by the nature of the acid, and the figures for the different acids are not strictly comparable.

To study the characteristic differences between these soils, we have, therefore, determined P_2O_5 -pH curves for different acids separately, namely for hydrochloric acid, lactic acid and citric acid of different strengths.

Extraction by hydrochloric acid of different strengths

In the first place we determined phosphate solubility for these three types of soil in hydrochloric acid of different strengths, shaking 5 gr of soil with 50 cc of liquid for two hours at room temperature and determining the end-pH of the mixture. The figures are found in Table II and depicted in Fig. 1—4; the curves are fairly regular and do not show marked undulations and maxima, but follow, as we will see, the well known course of logarithmic curves.

There is a marked difference in type between the three sets of curves. The moorcolonial soil with its large phosphate solubility, shows (Fig. 1) only a moderate decrease in phosphate solubility as the acidity of the extraction liquid decreases, and a considerable vertical distance between the curves at higher pH; a type as one might expect for a soil with little phosphate fixation and good solubility also at higher pH. We add that, for this soil with a P-unit of 15 (see Table I), 1000 kg of added P_2O_5 mean a theoretical increase in the phosphate figures of 66.7, so that a certain amount of phosphate fixation is apparent from Fig. 1 and Table II.

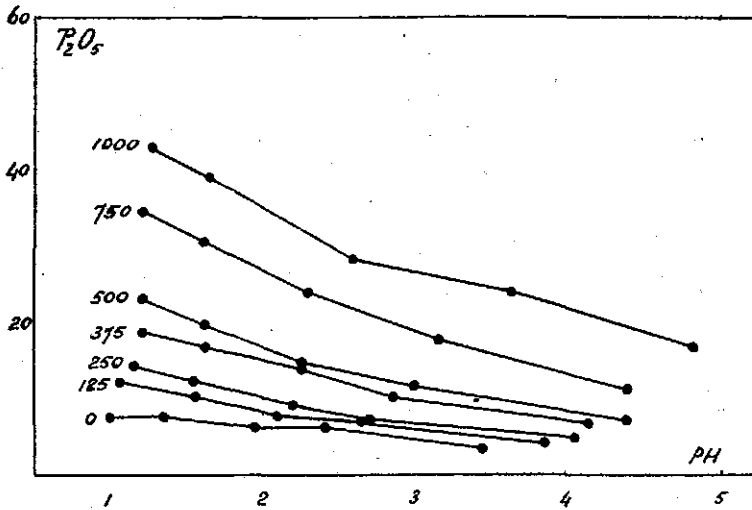


Fig. 1. Phosphate solubility in hydrochloric acid of different strengths, for plots with increasing amounts of phosphate of experiment field Pr. 87 on moorcolonial soil, plotted against end pH of the extraction liquid.

Phosphatlöslichkeit in Salzsäure verschiedener Verdünnungen für verschiedene Phosphatstaffeln des Versuchsfeldes Pr. 87 auf moorkolonialem Boden. Abszisse: End-pH der Extraktionsflüssigkeit.

For the sandy soil (Pr 113, Figs 2 and 3) the figures for P-number are, in the slightly acid extracts, much lower, only 10 or less, even after large applications of phosphate. In the acid extracts they rise to very high values, up to 130 for the plots that had received 2700 kg/ha P₂O₅ in the course of four years (in three applications). This soil, therefore, shows considerable phosphate fixation at the higher pH's, that is in ordinary soil.

The iron containing sand of Heino (Fig. 4) shows a similar picture: only very large applications, such as 2700 and 3600 kg/ha P₂O₅, have sufficiently saturated the power of fixation for phosphate of the soil, so that higher figures for phosphate solubility in slightly acid extracts result. The increase in phosphate solubility in the more acid extracts, which dissolve part of the fixed or difficultly available phosphate, is considerable, but not so large as in the case of the sandy soil.

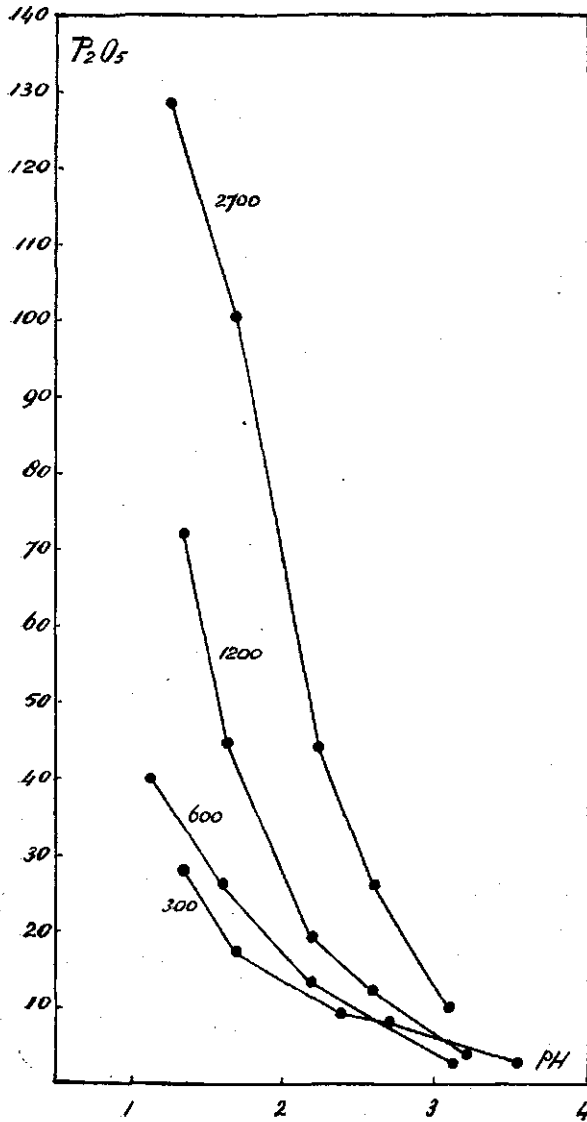


Fig. 2.

Phosphate solubility in dilute hydrochloric acid of different strengths, as in Fig. 1. for unlimed plots with increasing amounts of phosphate on experiment field Pr. 113, sandy soil.

Phosphatlöslichkeit in verdünnter Salzsäure wie in Fig. 1, für verschiedene Parzellen des Versuchsfeldes Pr. 113 (sandiger Boden), ungekalkte Parzellen mit steigenden Phosphatgaben.

Table II
Extraktion by different amounts of hydrochloric acid. Extraktion mit verschiedenen Mengen Salzsäure

Norma- lity of HCl	pH extra- ction liquid	Pr 87, moorcolonial soil				Pr 113, Sandy soil, unlimed				Pr 113, Sandy soil, limed				Heino, iron containing sandy soil											
		end pH sus- pension	P- figure	end pH sus- pension	P- figure	end pH sus- pension	P- figure	end pH sus- pension	P- figure	end pH sus- pension	P- figure	end pH sus- pension	P- figure	end pH sus- pension	P- figure	end pH sus- pension	P- figure								
		125 kg/ha P ₂ O ₅				250 kg/ha P ₂ O ₅				375 kg/ha P ₂ O ₅				500 kg/ha P ₂ O ₅				750 kg/ha P ₂ O ₅				1000 kg/ha P ₂ O ₅			
0.2	0.9	1.0	7 1/4	1.05	12	1.15	14	1.2	18 1/2	1.2	14	1.2	18 1/2	1.2	23	1.2	34 1/2	1.25	42 1/2						
0.05	1.3	1.35	7 1/2	1.55	10	1.55	12	1.6	16 1/2	1.6	12	1.6	16 1/2	1.6	19 1/2	1.6	30 1/2	1.65	39 1/2						
0.01	2.0	1.95	6	2.1	7	2.2	9	2.25	13 1/2	2.25	9	2.25	13 1/2	2.25	14 1/2	2.3	24	2.6	28						
0.005	2.3	2.4	6	2.7	6 1/2	2.75	7	2.85	10	2.85	7	2.85	10	3.0	11 1/2	3.15	17 1/2	3.65	24						
0.001	3.0	3.45	3 1/4	3.85	5	4.05	4 1/2	4.15	6 1/4	4.15	5	4.15	6 1/4	4.4	7	4.4	11	4.85	16 1/2						
		no phosphate				no phosphate				no phosphate				no phosphate				no phosphate							
		300 kg/ha P ₂ O ₅				600 kg/ha P ₂ O ₅				1200 kg/ha P ₂ O ₅				2700 kg/ha P ₂ O ₅											
0.2	0.9	1.35	28	1.15	40	1.35	72	1.25	128	1.25	40	1.25	128	1.25	40	1.25	128								
0.05	1.3	1.7	17	1.6	26	1.65	44	1.7	100	1.7	26	1.7	100	1.7	26	1.7	100								
0.01	2.0	2.4	9	2.2	13	2.2	19	2.25	44	2.25	13	2.25	44	2.25	13	2.25	44								
0.005	2.3	2.75	8	2.55	9	2.6	12	2.6	26	2.6	9	2.6	26	2.6	9	2.6	26								
0.001	3.0	3.6	2 1/2	3.15	2 1/2	3.25	3 1/2	3.1	10	3.1	2 1/2	3.1	10	3.1	2 1/2	3.1	10								
		no phosphate				no phosphate				no phosphate				no phosphate				no phosphate							
0.2	0.9	1.3	28	1.15	40	1.05	88	1.15	128	1.15	40	1.15	128	1.15	40	1.15	128								
0.05	1.3	1.7	16	1.6	26	1.6	64	1.6	104	1.6	26	1.6	104	1.6	26	1.6	104								
0.01	2.0	2.35	9	2.4	10	2.35	26	2.4	50	2.4	10	2.4	50	2.4	10	2.4	50								
0.005	2.3	2.9	5	2.7	7	2.75	15	2.8	24	2.8	7	2.8	24	2.8	7	2.8	24								
0.001	3.0	3.9	1 3/4	3.55	2 1/2	3.9	4 1/2	3.85	10	3.85	2 1/2	3.85	10	3.85	2 1/2	3.85	10								
		no phosphate				no phosphate				no phosphate				no phosphate				no phosphate							
0.2	0.9	0.75	12	1.05	17	0.7	22 1/2	0.8	31	0.8	17	0.8	31	0.8	17	0.8	31	0.95	46						
0.05	1.3	1.7	7	1.8	7 1/2	1.5	12	1.7	15	1.7	7	1.7	15	1.75	17 1/2	1.75	22	1.8	28						
0.01	2.0	2.55	5	2.7	5 1/2	2.75	7 1/2	2.75	8 1/2	2.75	5 1/2	2.75	8 1/2	2.8	10 1/2	2.8	13	2.95	24						
0.005	2.3	3.4	4	3.6	4	3.55	6	3.65	5	3.65	4	3.65	5	3.9	6	3.9	9	4.05	17						
0.001	3.0	5.3	1	5.15	1 1/2	5.0	1 1/2	5.15	2	5.15	1 1/2	5.15	2	5.35	1 1/4	5.35	4 1/4	5.3	7 1/2						

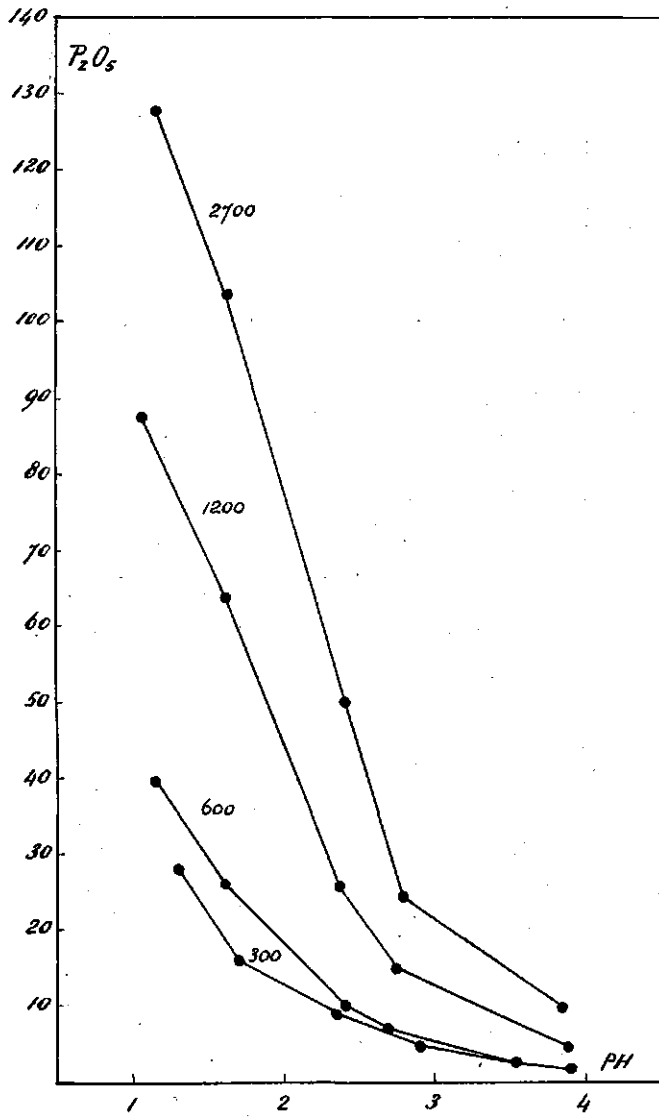


Fig. 3. Phosphate solubility as in Fig. 2, for limed plots of the same experiment field.

Phosphatlöslichkeit wie in Fig. 2, für gekalkte Parzellen desselben Versuchsfeldes Pr. 113 (sandiger Boden).

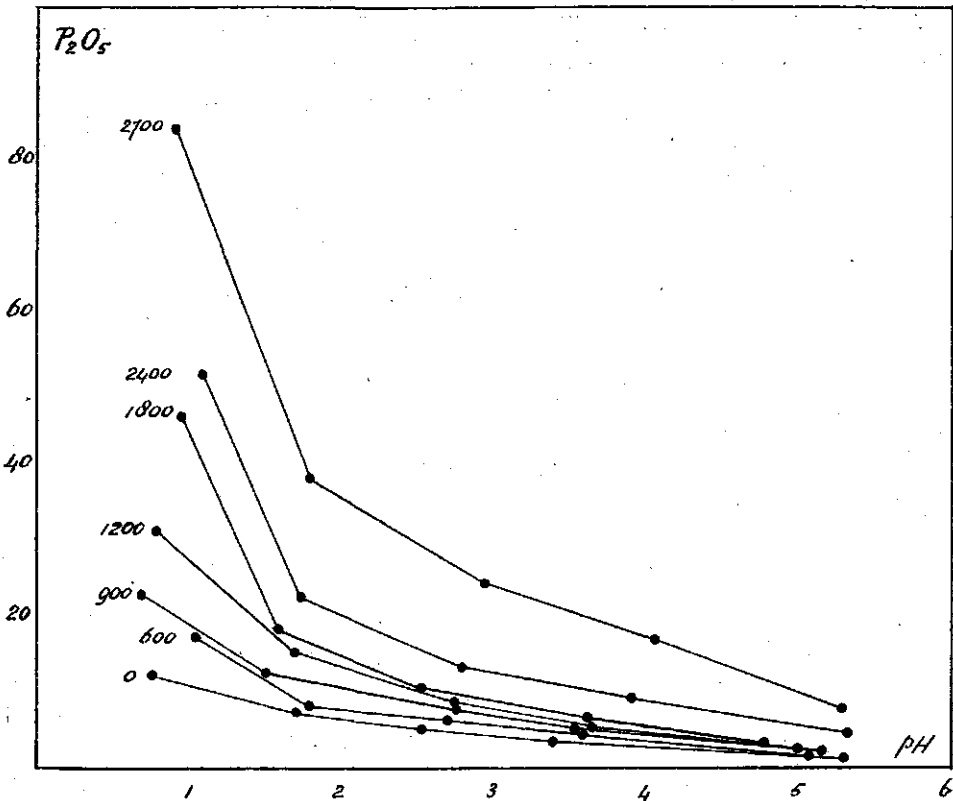


Fig. 4. As Fig. 1—3, for the iron-containing sandy Heino soil.
Wie Fig. 1—3, für den eisenhaltigen Sandboden aus Heino.

As a whole, the course of the HCl-extraction curves strikes one as very regular and simple, compared with those obtained for Norwegian types of soil by T. Gaarder and O. Grahl-Nielsen⁸⁾ (extraction 1: 20 by mixtures of water and 0.1 n HCl or 0.1 n NaOH during four days): in our three types of soil the phosphate solubility increases gradually with increasing acidity, without the minima and undulations found by Gaarder and Grahl-Nielsen. The curves, found for five samples of New Zealand soils by H. O. Askew⁹⁾, have below pH 6 a similar simple type as ours; these samples show increasing phosphate solubility at higher pH (obtained by addition of NaOH), a part of the curve that was not investigated by us.

⁸⁾ T. Gaarder und O. Grahl-Nielsen, Medd. Nr. 18, Vestlandets Forstlige Forsøksstation, Bergen 1935, p. 92—94.

⁹⁾ H. O. Askew, N. Zealand Journ. of Science and Technology 16, 145 (1934).

The solubility curves, in our case, have nearly the form of the logarithmic curve. Fig. 5 and 6 show that, plotted logarithmically, nearly straight lines are obtained. Moreover, for different amounts of phosphate on the same soil, these logarithmic lines run parallel to each other; but the sets for the three types of soil show a different slope.

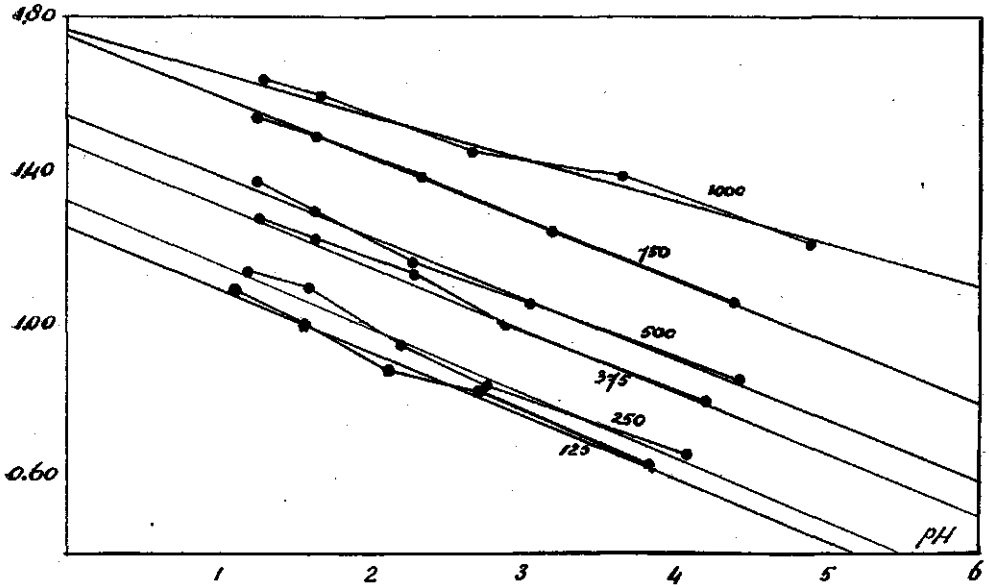


Fig. 5. Logarithmic curves (log. of phosphate in HCl against end pH of mixture) for different plots (increasing amounts of phosphate) of Pr. 87, moorcolonial soil.

Logarithmen von Phosphatlöslichkeit in Salzsäure von verschiedenen Verdünnungen, gegen End-pH der Flüssigkeit, für den moorkolonialen Boden aus Fig. 1. Die Linien sind nahezu gerade und, mit Ausnahme derer von der Parzelle mit 1000 kg/ha P_2O_5 , einander parallel.

As an example we represent in Fig. 5 the logarithmic curves for the moorcolonial soil of Pr 87, in which only the upper curve (1000 P_2O_5) has a somewhat deviating slope. Fig. 6 depicts the average curves for the limed and the unlimed plots of the sandy soil (Pr 113): small experimental errors are eliminated by taking the two cases together, and we get curves which very nearly run parallel to each other, but with a much steeper slope than those in Fig. 5. We postpone a closer study of the relatively simple relationships, that present themselves from these graphs, till a larger material, from different types of soil, has been collected.

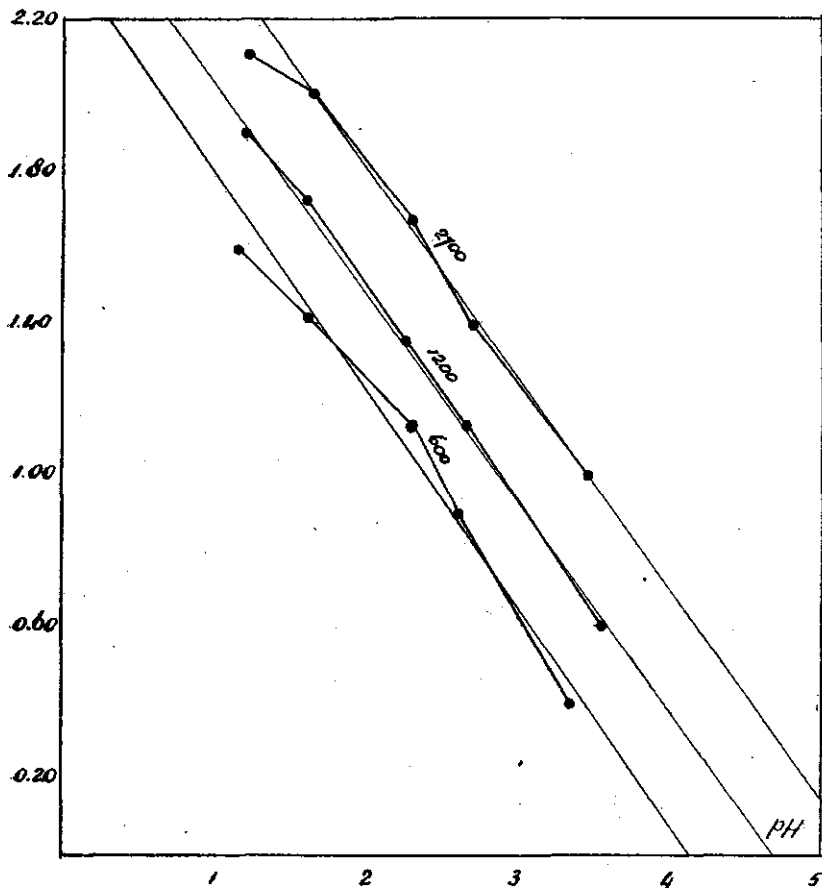


Fig. 6. Logarithmic curves (log. of phosphate in HCl), averages of the limed and the unlimed plots of Pr. 113 (Figs. 2 and 3).
 Logarithmen wie in Fig. 5, für Mittelzahlen aus den Figuren 2 und 3, sandigem Boden von Versuchsfeld Pr. 113.

Comparison of solubility in different acids

To proceed in a systematic way, we have compared the solubility in citric acid and that in lactic acid with the HCl-solubility curves described above, for one of the phosphate amounts of each type of soil, using for all three acids the same method of extraction (5 gr soil and 50 cc liquid, shaken for two hours at room temperature). The object, chosen for each soil, was one that represented a reasonable phosphate supply. The results are given in Table III and depicted in Figs 7—10. We added the figures for our usual extracts (P-number and P-citr); as the P-number is determined in a different way (24 hours at 50° C),

Table III
 Extraktion by different acids
 Extraktion von je einer Bodenprobe pro Bodentyp, mit verschiedenen Extraktionsmethoden,
 siehe Table IV

Objekt	hydrochloric acid		lactic acid		citric acid		P- numb.	P- citr.	P- water,	P- Egn	P- Truog	P- Bond.	P- Amm. acet.	
	0.01 n	0.005 n	0.1 n	0.01 n	1 %	0.01 %								0.001 %
Pr 87, 800 P ₂ O ₅	2.35 14	2.8 10½	2.4 19½	3.25 10½	2.45 20	4.5 9½	5.0 6¼	5.25 7½	2.3 21	5.1 5¾	3.55 15	3.0 28	2.5 11	4.6 9½
Pr 118, unlimed, 1200 P ₂ O ₅	2.2 19	2.6 12	2.55 30	2.95 6	2.4 43	3.7 7½	4.35 2½	4.75 4	2.25 52	4.55 2	3.5 26	3.05 39	2.5 26	4.6 8
Pr 113, limed, 1200 P ₂ O ₅	2.35 26	2.75 15	2.55 36	3.1 7	2.45 56	4.15 8	5.2 3½	5.35 7	2.2 61	5.45 4	3.5 29	3.0 52	2.5 39	4.6 8
Heino, 1800 P ₂ O ₅	2.55 10½	3.65 6½	2.5 12	3.65 6½	2.4 50	3.45 12	4.75 4	6.5 5	2.4 51	5.85 2¾	3.7 25	3.05 52	2.5 12½	4.6 12
Versuchsobjekt	Salzsäure		Milchsäure		Zitronensäure		P- Zahl	P- Zitr	P- Wass.	P- Egn	P- Truog	P- Bond	P- Amm. acet.	

we also determined phosphate solubility in water (P-water) after shaking two hours at room temperature. In Table III and Figs 7—10 we further added the figure obtained according to the calcium lactate — hydrochloric acid buffer methode of Egnér¹⁰) (P-Egn), the Truog-method¹¹), the nitric acid extraction according to Bondorff and Steenbjerg¹²), and an extraction by an ammonium acetate — acetic acid buffer with pH 4.6, which we use in our work. The P-figures are plotted in each case against the end-pH of the mixture and not against the pH of the extraction liquid. To facilitate a comparison, we give a brief review of the principal points in the different methods of testing in Table IV; besides the extraction medium, there are differences in quantity of liquid, duration and temperature of extraction, that are undoubtedly responsible for part of the differences in P-figures.

It will be seen from Figs 7—10 that for the iron containing sand (Fig. 10) the curve for lactic acid practically coincides with that for hydrochloric acid; the sandy soil of Pr 113 (Figs 8 and 9) and the moor-colonial soil (Fig. 7) give, at lower pH, higher P-figures with lactic acid than with hydrochloric. Citric acid gives higher figures in all cases, with the exception, perhaps, of the iron containing soil at higher pH. It may be assumed that, while lactic and hydrochloric acid act in about the same way, the pH (correctly speaking, the H⁺-ions) being the active agent, other reactions come into the play with citric acid, the formation of complex phosphate compounds or complex iron compounds perhaps playing a role and causing the higher phosphate figures.

Our usual determination of P-citr differs from the figures discussed above in that the extraction is continued for 27 hours, shaking the extraction bottles at first during 2 hours, leaving them at room temperature for about 24 hours and finally shaking during 1 hour in the machine, before drawing of the liquid. In general, higher phosphate solubility figures may be expected from this treatment than those mentioned above, obtained after two hours shaking; this is indeed the case for all four soils. This difference between citr and P-citr is largest in the case of the sandy soil (Pr 113); whether this is connected with the difference in phosphate solubility in lactic and hydrochloric acid

¹⁰) H. Egnér. Metod att bestämma lättlöslig fosforsyra i åkerjord. Medd. No. 425 från Centralanstalten för försöksväsendet på jordsbruksområdet, 1932, p. 30.

¹¹) E. Truog. J. Am. Soc. Agron. 22, 874 (1930). The determination of readily available phosphorus in soils.

¹²) K. A. Bondorff og F. Steenbjerg. Tidsskrift for Planteavl 38, 273 (1932). Studier over Jordens Fosforsyreindhold. I. Jordfosforyrens Opløselighed.

Table IV.
Principal points in the different methods of extraction
Vergleich zwischen den wichtigsten Punkten bei den verschiedenen
Extraktionsmethoden

Abbreviation	Sign.	Extraktion liquid	pH of same	Ratio soil : solution	Duration	Temperature	
HCl	×	Hydrochloric acid, 0.01 n	2.0	1:10	2 hours	room	Salzsäure
		„ „ 0.005 n	2.3	1:10	„	(Zimmer)	„
		„ „ 0.001 n	3.0	1:10	„	„	„
Lact	+	Lactic acid, 0.1 n	2.1	1:10	2 hours	room	Milchsäure
		„ „ 0.01 n	2.9	1:10	„	„	„
		„ „ 0.001 n	4.3	1:10	„	„	„
Citr	•	Citric acid, 1% ₀	2.1	1:10	2 hours	room	Zitronensäure
		„ „ 0.01% ₀	3.25	1:10	„	„	„
		„ „ 0.001% ₀	3.9	1:10	„	„	„
P-water	○	Water	5.7	1:10	2 hours	room	Wasser
P-number	□	Water	5.7	1:10	24 hours	50° C	Wasser
P-citr	∅	Citric acid, 1% ₀	2.1	1:10	2+24+1 hours	room	1% ₀ Zitronensäure
P-Egn	△	Egnèr-liquid, Ca-lactate 0.02 n HCl 0.01 n	3.5—3.6	1:50	2 hours	room	Kalziumlactat—HCl nach Egnèr
Tr	■	0.002 n H ₂ SO ₄ + (NH ₄) ₂ SO ₄ (Truog)	3.0	1:200	1/2 hours	room	Schwefelsäure — Ammonsulfat nach Truog
Bo	○	HNO ₃ div conc. (Bondorff)	div	1:25	3 hours	room	Salpetersäure nach Bondorff
Amm	⊗	0.2 n ammon. acetate + 1 vol 0.2 n acetic acid	4.6	1:10	2 hours	room	Ammoniumacetat und Essigsäure
Abkürzung	Zeichen	Extraktionsflüssigkeit	pH derselben	Verhältnis Boden zu Flüssigk.	Zeitdauer der Extraktion	Temperatur der Extraktion	Extraktionsflüssigkeit

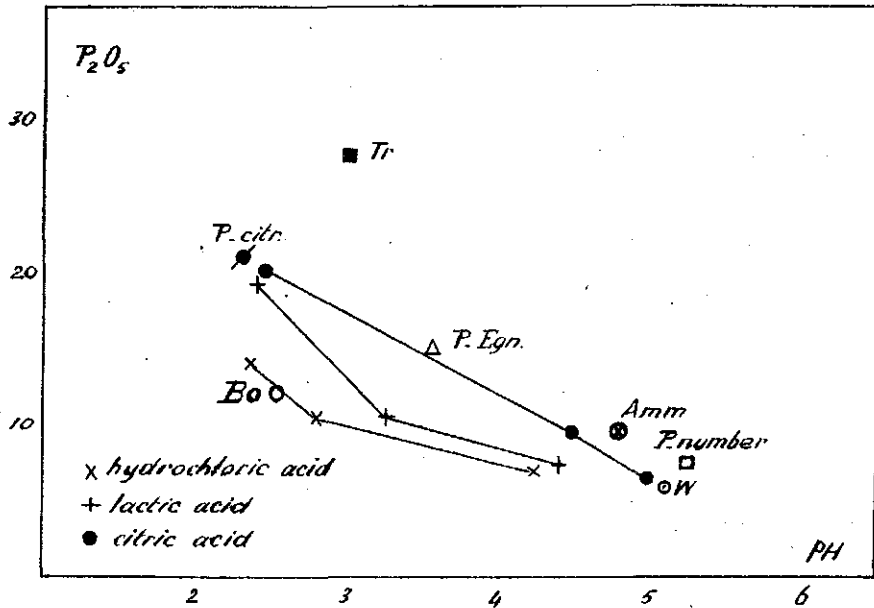


Fig. 7. Phosphate solubility for one plot (800 P₂O₅) of Pr. 87 in different acids, using different strengths for hydrochloric, lactic and citric acid, see tables II and IV.

Phosphatlöslichkeit für eine Parzelle von Pr. 87 (800 P₂O₅) in verschiedenen Säuren bei verschiedenem PH: Salzsäure (x), Milchsäure (+) und Zitronensäure (●).

Daneben P-Zitr. (P-citr.) und P-Zahl (P-number) nach unserer gewöhnlichen Methode, P-Egnèr, P-Bondorff, P-Truog, P-Ammoniumazetat und P-Wasser, siehe Tabelle IV.

stated above, can only be considered when a comparative study of a much larger number of examples has been made.

The P-number (squares in Figs 7—10) is determined in ordinary distilled water, containing some carbonic acid and showing a pH of about 5.7—5.8; the mixture is shaken during a short time by hand and then kept at a temperature of 50° C for 24 hours. The P-number may therefore be expected to be higher than the figure for the water extract after two hours shaking (W in Fig. 7—10); this is indeed the case with all four samples.

It will further be seen from Table III and Figs 7—10 that the Egnèr buffer solution (P-Egn. in the figures; extraction during two hours at room-temperature — not exactly 20° C, as prescribed by Egnèr — with constant shaking on the machine; pH of the mixture 3.5—3.6) gives a much higher phosphate solubility than is the case with lactic acid

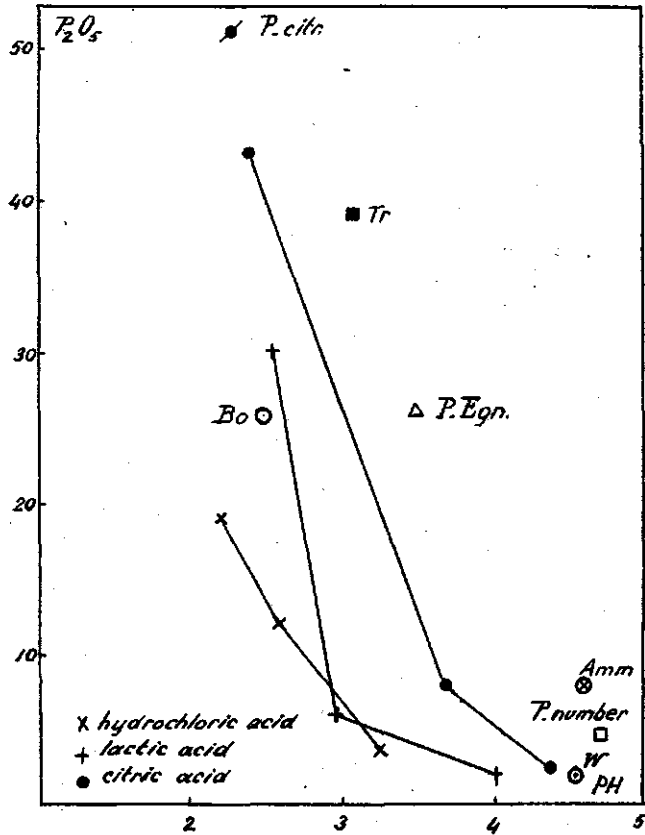


Fig. 8. Phosphate solubility in different acids, as in Fig. 7 for one unlimed plot (1200 P_2O_5) of Pr. 113. Phosphatlöslichkeit in verschiedenen Säuren und nach verschiedenen Methoden bestimmt, eingebracht nach End-pH der Extraktionsflüssigkeit, für eine ungekalkte Parzelle (mit 1200 P_2O_5) von Versuchsfeld 113 auf sandigem Boden.

or hydrochloric acid at the same pH, and also higher than citric acid. The reason for this behaviour will have to be sought in the first place in the larger quantity of extraction liquid (50 to 1); in how far complex formation, which Egnèr considers desirable in phosphate determination in soils, or other special factors play a role, would have to be investigated by making a comparison with other acids or buffer solutions, using the same ratio of liquid to soil.

A similar remark holds for the figures obtained according to Truog's method, in which the largest ratio of liquid to soil (200 : 1) is used and which gives higher figures than citric acid.

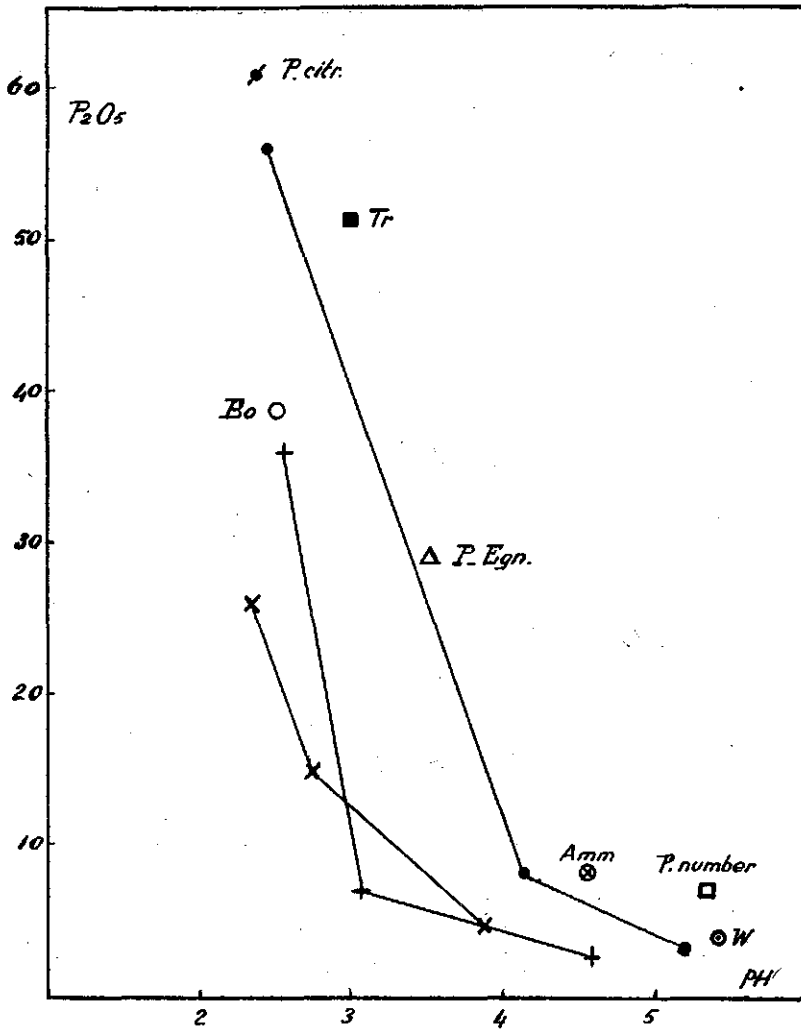


Fig. 9. As Fig. 8, for the limed plot with 1200 P_2O_5 .
 Wie Fig. 8, für die gekalkte Parzelle mit 1200 P_2O_5 .

Nitric acid extraction at pH 2.5, according to Bondorff and Steenbjerg's method, gives figures which fall in the neighbourhood of the hydrochloric and the lactic acid curves, mostly practically coinciding with the latter. The ammonium acetate — acetic acid buffer solution at pH 4.6 gives in all four cases higher figures than citric acid (same ratio, same duration and temperature).

Taken as a whole, five figures (P-citr, Truog, P-Egnèr, Amm and P-number) fall practically in a curve or zone that follows approximately

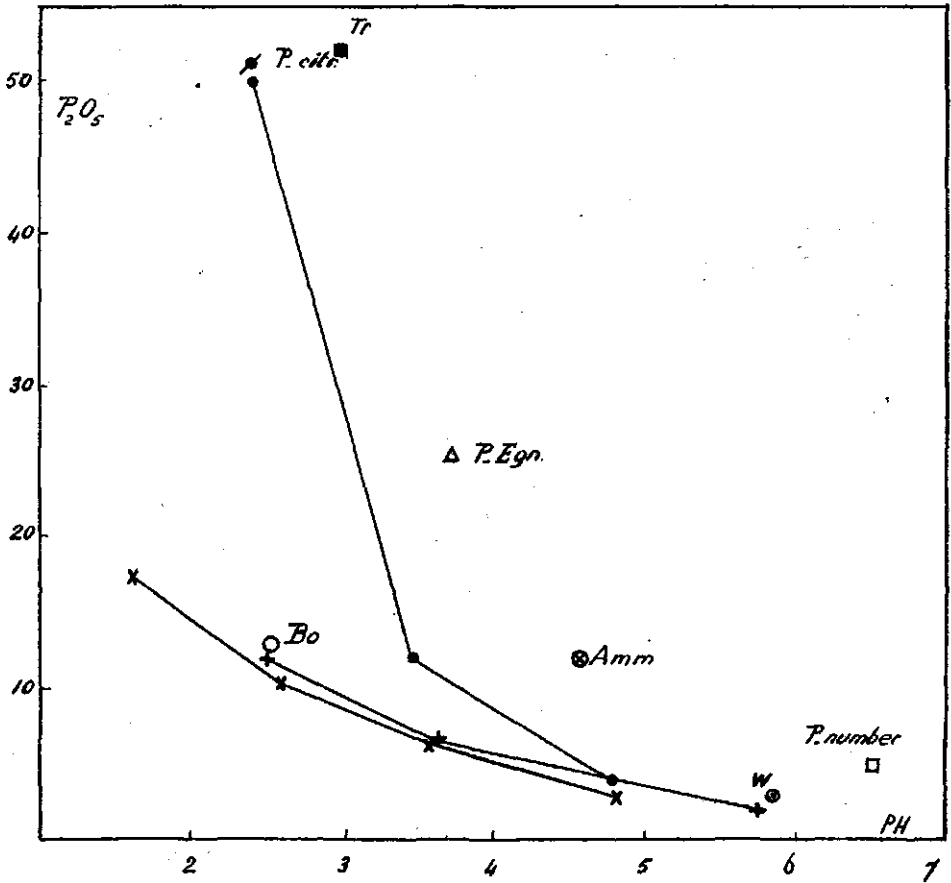


Fig. 10.

Same as Fig. 7—9 for one plot (1800 P₂O₅) of the iron-containing sandy Heino soil. Selbe Daten wie in Fig. 7—9 für eine Parzelle vom eisenhaltigen Sandboden von Heino.

the same course as those for extraction during two hours by increasing amounts of citric acid, but lies somewhat higher.

When this should be the case, not only in the four examples treated in this paper, but in general, this would mean that these methods teach us about the same thing when only the right correction for pH of the end-mixture could be applied. Only in the case of Pr 87 (Fig. 7) is the Truog-figure found considerably higher than the zone in which the other four lie. This would mean that in such a case the Truog method gives quite another indication about the phosphate status of the soil than the Egnèr-method or our P-citr and P-number method. Which of the two pictures is the most correct in such a case, or rather the most useful

from the standpoint of the agricultural adviser, will have to be decided by means of experimental fields, as will be discussed later on.

Further light can be thrown on this point by the samples used for the Königsberg comparison, in so far as these represented light soils in which we applied our methods of phosphate determination. The results for 22 samples are plotted in Fig. 11; it will be seen that, taken as a whole, P-citr, P-Truog, P-Egnèr and P-number follow for each sample a similar course as in Fig. 8—10. Some deviations occur; it would have to be investigated whether these are relevant and represent characteristic properties of the soils in question. It may be pointed out that the end-pH for the Truog figures is taken at 3 for all samples; it would have to be controlled whether in cases such as Nos 9 and 16 (for which the pH-water is 7.4 and 7.2 respectively) this represents the actual state of the extract.

Other substances, dissolved by citric and lactic acid

In accordance with point b of the Königsberg desiderata (see page 65) we made some determinations of the amount of Ca, Mg, Fe + Al and Si dissolved by citric and by lactic acid, to get a preliminary idea in how far this may offer an explanation of the differences in phosphate solubility. The figures may be found in Table V. A closer study of the question, in how far the "other substances" cause or explain a difference in phosphate figures, will have to be postponed till more experimental material is available; at first sight the following points draw the attention.

The difference between the citric and the lactic acid curves (Figs 7 to 10) is greatest in the iron containing sand (Fig. 10), especially at pH 2—3. This coincides with the greatest difference in $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ dissolved at pH $2\frac{1}{2}$ (119 against 28), the amount of CaO + MgO being about the same (226 against 231). At pH $3\frac{1}{2}$ the difference in phosphate solubility is much smaller, and it disappears at higher pH: the course of iron-aluminium solubility is the same. The high figure for dissolved CaO in 0.01 n lactic acid (116) as compared with citric ($21\frac{1}{2}$) is striking; the same ratio is, however, found in the other soils (Pr 87 and Pr 113 limed, not in Pr 113 unlimed).

The difference in iron + aluminium in the extract of pH about $2\frac{1}{2}$ is 75 and 71 for the sandy soil of Pr 113, unlimed and limed; therefore smaller than in the Heino soil. The difference between phosphate in citric and in lactic acid is also much smaller. In the moorcolonial soil of Pr 87 the figures for iron + aluminium are 50 and 24 or a difference

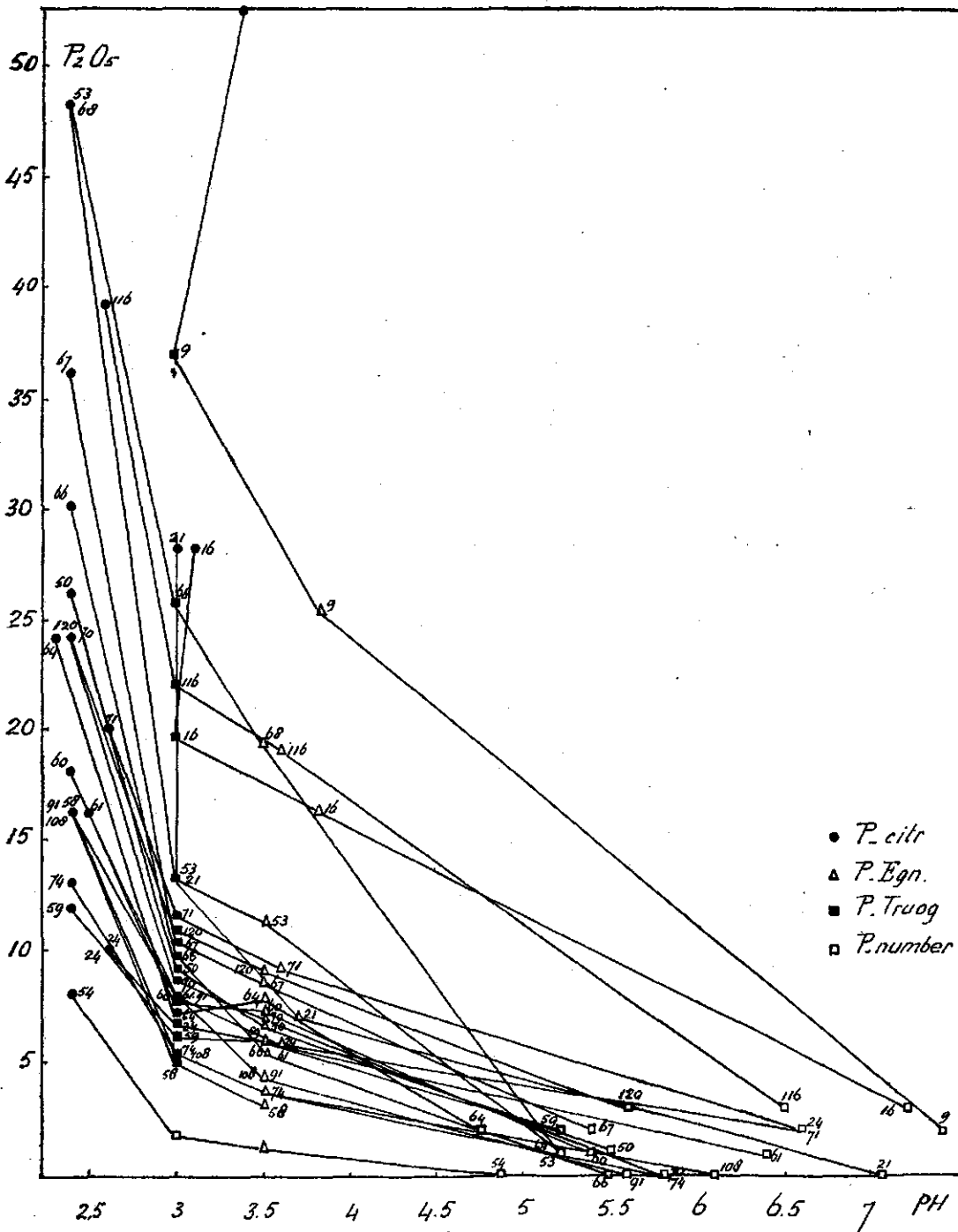


Fig. 11. P -citr, P -Truog, P -Egnèr and P -number for 22 samples of light soil from the Mitscherlich Gemeinschaftsarbeit, plotted against pH of the extract.

P -Zitr, P -Truog, P -Egner und P -Zahl für 22 Proben von leichten Böden aus der Mitscherlich'schen Gemeinschaftsarbeit, gegen pH des Extraktes. Für jede Probe haben die Verhältnisse einen ähnlichen Zusammenhang wie in Fig. 8—10, obgleich hier und da Abweichungen vorkommen.

Table V
 Substances (mg per 100 g soil), dissolved by citric and lactic acid of different strength from the four soils
 Substanzen (mg per 100 g Boden) im Zitronen- bzw. Milchsäure-Auszug der vier Böden bei verschiedener Säurekonzentration

	Pr 87, 800 P ₂ O ₅			Pr 113, unlimed, 1200 P ₂ O ₅			Pr 113, limed, 1200 P ₂ O ₅			Heino, 1800 P ₂ O ₅		
	SiO ₂	Fe ₂ O ₃ + Al ₂ O ₃	MgO	SiO ₂	Fe ₂ O ₃ + Al ₂ O ₃	MgO	SiO ₂	Fe ₂ O ₃ + Al ₂ O ₃	MgO	SiO ₂	Fe ₂ O ₃ + Al ₂ O ₃	MgO
1% citric acid	6	50	12	24	176	11	26	192	20	13	119	29
0.01% citric acid	13	29	3	4	22	8	4	26	13	6	26	14
0.001% citric acid	18	9	1	3.5	1	4	4	1	5	3.5	5	1
0.1 n lactic acid	26	24	8	15	101	38	17	121	15	7.5	28	29
0.01 n lactic acid	8	5	6	5	4	21	6	3	10	6	8	7
0.001 n lactic acid	13	1	3	3	1	11	4	1	9	6.5	4	0

of 26, coinciding with practically no difference in phosphate dissolved in the citric and the lactic extracts.

At pH about $3\frac{1}{2}$ the differences in the sesquioxides are 18 and 23 for the sandy soil; at pH $4\frac{1}{2}$ the difference is 28 for the moorcolonial soil; the difference in phosphate figures is only a few units.

Suitability of the different methods for judging the fertiliser requirement of the soil

It is one thing to state a difference in the behaviour of different types of soil, when they are treated by different acid extraction media, but quite another and a much more complicated thing to say, what is the significance of such a difference in behaviour from an agricultural point of view and what it means in advice work on manuring. For this latter purpose the picture, obtained by chemical investigation, must be brought into correlation with agricultural points of view obtained from practical experience and from field experiments or pot cultures. In the three cases, to which the above investigations relate, we know the phosphate regime from the results of field experiments, in which different phosphates in different quantities were added yearly or with intervals (to study the after-effect). We have described the picture that our usual methods of testing (P-number, P-citr, and occasionally P-total and P-fixation) give of the phosphate supply and requirement of the crop in the publications indicated above. One of the results of our comparison was that citric acid gives much higher figures at the same pH than lactic and hydrochloric acid in the case of the iron containing sand at lower pH, but very much less so for the moorcolonial soil and the heath sand. Whether this fact represents a general characteristic feature, can only be said when an appropriate number of cases has been investigated and compared. And even if citric acid should be found always to dissolve from iron containing sand more phosphate than the other two acids, the all-important question from an agricultural point of view is whether this picture, obtained by citric acid, gives us a better basis for agricultural advice work — that is to say whether it represents the reaction of the plant more closely and more correctly — than the other acids, or not. To solve this point, a sufficient number of cases (preferably field experiments) of known phosphate regime will have to be studied and compared from this point of view.

Summary

In three types of light soil (a moorcolonial soil, a sandy heath reclamation soil, and an iron containing sandy soil) phosphate solubility was investigated with different acids (hydrochloric, lactic and citric) at different strengths, and also according to different methods (Egnèr, Truog, Bondorff and Steenbjerg, ammonium acetate buffer). The results are brought together in Figs 7—10, plotted against pH of the extract, which is found to play a prominent role in the results. The ratio soil: extraction liquid and other circumstances (duration and temperature of extraction, see Table IV) and the characteristics of the acid play a further role.

The figures found by the Egnèr and the Truog methods lie, with our P-citr and P-number, and also the ammonium acetate buffer extract figure, in one zone or curve, which lies somewhat higher than that for the citric acid extracts. When the influence of pH is eliminated, these methods therefore seem to teach us the same things. A similar relationship is found in 22 soil samples of the Königsberg comparative testing (Fig. 11).

The nitric acid extract according to Bondorff and Steenbjerg gives a figure which coincides approximately with hydrochloric and lactic acid extracts of the same end pH; this group of figures is lower than those for the citric acid extracts.

The phosphate solubility curves for hydrochloric acid of different strengths show a logarithmic form; plotting logarithms of dissolved P_2O_5 against pH, straight lines are obtained which run parallel for plots of the same field manured with increasing quantities of phosphate. The slope of these lines are different for the three soil types.

In extracts obtained by citric and lactic acid of different strengths, different substances were determined. There was some parallelism between the difference in dissolved iron + aluminium and the difference in phosphate figure in the two acids. There were some striking differences in the course of CaO solubility, which did not, however, seem to be in relationship with phosphate solubility.

Zusammenfassung

Löslichkeit von Phosphat bei drei leichten Bodentypen
in verschiedenen Säuren und bei verschiedenem pH

VON

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Die Mitscherlich'sche Gemeinschaftsarbeit verlangte, wie im überaus interessanten Bericht¹⁾ über die Königsberger Konferenz (1936) auseinandergesetzt wird, ein näheres, systematisches Studium der Phosphatlöslichkeit in verschiedenen Säuren und bei verschiedenen pH-Staffeln, und weiter eine Untersuchung über die Substanzen, welche in diesen verschiedenen Extrakten, neben Phosphat, gelöst werden.

Als Beitrag zu diesem Problem wurde die Phosphatlöslichkeit in Zitronensäure, Milchsäure und Salzsäure untersucht bei drei verschiedenen leichten Böden, deren Phosphathaushalt durch ausführliche Untersuchungen bei Feld- und Topfversuchen bekannt war, und zwar ein moorkolonialer Boden²⁾, ein neu urbar gemachter Heidesandboden³⁾ und ein eisenhaltiger Sandboden⁴⁾. Einige Daten über diese Böden sind in Tabelle I enthalten; eine Betrachtung über den Zusammenhang zwischen P-Zahl und P-Zitr, bzw. P-Zitr und P-Total wurde an anderer Stelle⁵⁾ gegeben, wobei es sich herausstellte, daß für ein und denselben Boden der Zusammenhang fast gradlinig ist, und daß, nach End-pH der Extraktionsflüssigkeit zusammengestellt, die Punkte für jeden Bodentyp charakteristische Kurven bilden. Diese Kurven haben jedoch nur orientierende Bedeutung, da die verschiedenen Säuren in verschiedener Weise einwirken können (Komplexbildung, In-Lösung-Bringen von anderen Bestandteilen usw.). Es wurden darum zunächst Löslichkeitskurven in Salzsäure von verschiedenen Verdünnungen bestimmt für verschiedene

¹⁾ Erster Bericht über die Arbeiten und über die Tagung der Arbeitsgemeinschaft zur Prüfung der Laboratoriumsmethoden für die Bestimmung des Kali- und Phosphorsäurebedürfnisses der Böden, Königsberg 12.—19. Juli 1936. Zu erhalten von Dr. D. J. Hissink, Groningen, fl. 4.—

²⁾ O. de Vries und C. W. G. Hetterschij: Der Phosphorsäure-Haushalt in moorkolonialem Boden. Die Phosphorsäure 5, 46 (1935).

³⁾ O. de Vries und C. W. G. Hetterschij: Der Phosphorsäure-Haushalt im Heidesandboden (1935). Exemplare erhältlich bei der Rijkslandbouwproefstation, Groningen.

⁴⁾ O. de Vries und C. W. G. Hetterschij: Fosfaathuishouding in een ijzerhoudenden zandgrond (mit deutscher Zusammenfassung). Verslagen van Landbouwkundige Onderzoekingen 43, 171 (1937); den Haag, Landsdrukkerij.

⁵⁾ O. de Vries, C. W. G. Hetterschij und F. van der Paauw, Zeitschr. Bodenk. u. Pflanzen ern. 6 (51), 144 (1938).

Phosphatstaffeln der genannten drei Bodentypen; die Resultate sind in Fig. 1—4 abgebildet und in Tabelle II zusammengebracht. Es fällt auf, daß die Löslichkeitskurven sehr regelmäßig verlaufen, ohne die Minima und Wellen zu zeigen, welche T. Gaarder und O. Grahl-Nielsen (l. c.) fanden. Logarithmisch gegen pH ausgesetzt, sind die Kurven fast gradlinig, während die Linien für denselben Bodentyp einander praktisch parallel sind (Fig. 5 für Pr 87; Fig. 6 für Mittelzahlen von gekalkten und ungekalkten Parzellen von Pr 113).

Es läßt sich nun das Studium der Phosphatverhältnisse weiter ausbauen, indem man die Resultate vergleicht, welche unter gleichen Umständen mit verschiedenen Säuren erhalten werden, und diese in Zusammenhang bringt mit der Zusammensetzung der verschiedenartigen Extrakte, welche diese Säuren geben. Ein Vergleich zwischen der Geeignetheit von Milchsäure mit derjenigen von Zitronensäure z. B. wird sich mit der Möglichkeit der Bildung von komplexen Eisenverbindungen und deren Einfluß auf die Löslichkeit des Phosphat-Ions zu beschäftigen haben. Es liegt da noch ein großes Untersuchungsgebiet offen, das wertvolle Aufklärungen bringen könnte und das die Aufmerksamkeit einer größeren Zahl von Forschern verdient.

Das Verhalten gegen verschiedene Säuren verschiedener Stärke wurde nun für je eine Parzelle (Phosphatstaffel mit ausreichender Phosphatgabe) pro Bodentyp bestimmt und in Fig. 7—10 abgebildet; in diesen Figuren wurden außerdem die Zahlen für einige von den gebräuchlichen Extraktionsmethoden angegeben. Tabelle III gibt die erhaltenen Zahlen, Tabelle IV zeigt die Unterschiede bei der Ausführung der verschiedenen Methoden.

Salzsäure und Milchsäure, in derselben Weise angewandt, geben bei dem eisenhaltigen Sandboden (Fig. 10) und dem moorkolonialen Boden (Fig. 7) praktisch zusammenfallende Löslichkeitskurven; beim Heidesandboden fallen die Zahlen für verdünnte Extrakte zusammen, aber Milchsäure löst bei größerer Stärke mehr als Salzsäure.

Zitronensäure löst bei jedem pH mehr als die beiden anderen Säuren. Unsere P-citr-Zahl liegt immer etwas höher als die Zitronensäure-Kurve, wohl weil die Extraktionsdauer (27 Stunden gegen 2) länger und die Temperatur höher ist (vgl. Tabelle IV).

Das Kalziumlaktat-Salzsäure-Gemisch von Egnèr gibt merklich höhere Zahlen als Milchsäure, sogar meistens etwas und manchmal deutlich mehr als Zitronensäure.

Unsere P-Zahl (Wasser, 24 Stunden; P-number in Fig. 7—10) gibt etwas höhere Phosphatzahlen als eine zweistündige Extraktion mit Wasser (W in Fig. 7—10), wie zu erwarten war.

Die Phosphatlöslichkeit in einem Schwefelsäure-Ammonsäure Gemisch (200 Vol.) nach Truog ist derjenigen in 1% Zitronensäure ungefähr gleich; dagegen löst Salpetersäure (25 Vol.) bei pH 2.5 nach Bondorff und Steenbjerg in den vier Fällen ungefähr ebensoviel als Milchsäure bei demselben pH. Es ist klar, daß, neben pH der End-Mischung, das Verhältnis Boden: Extraktionsflüssigkeit eine bedeutende Rolle spielt.

Eine Ammoniumazetat-Essigsäure Puffermischung, welche wir bei unseren Untersuchungen manchmal benutzen, gibt bei pH 4.6 und bei denselben Extraktionsverhältnissen wie oben (1:10, zwei Stunden, Zimmertemperatur), Zahlen für die Phosphatlöslichkeit, welche mit der P-Zahl, P-Egnèr, P-Truog und P-citr ziemlich in eine Kurve oder Zone fallen, welche der Zitronensäure-Kurve parallel verläuft und etwas höher liegt. Die Unterschiede zwischen diesen Extraktionsmitteln scheinen daher in der Hauptsache durch das pH des Extraktes bestimmt zu werden, wobei etwaige Eigentümlichkeiten der Lösungsmittel durch die Wahl der Extraktionsbedingungen (Extraktionsverhältnis, Dauer, Temperatur) teilweise ausgeglichen sind.

Ähnliche Zahlen (P-citr, P-Truog, P-Egn und P-Wasser) für 22 leichte Böden aus der gemeinschaftlichen Untersuchung (Konferenzbericht 1936, Tabelle III Seite 118) zeigt Abb. 11; mit einigen Ausnahmen ist der Verlauf der Kurven ziemlich kongruent und denjenigen in Fig. 7 bis 10 ähnlich, so daß dieses Verhältnis der gegenseitigen Lage ziemlich allgemein vorzukommen scheint.

Nur beim moorkolonialen Boden von Pr 87 (Abb. 7) liegt die Truog-Zahl bedeutend höher als die anderen. Inwieweit dies für den betreffenden Bodentyp charakteristisch ist, wäre durch die Untersuchung von mehr Proben auszumachen. Welches Extraktionsmittel aber die Verhältnisse, wie die Pflanze sie empfindet, für alle Bodentypen am eindeutigsten und am schärfsten wiedergibt, wäre nur festzustellen an einem umfangreichen Material von Feldversuchen, in denen der Phosphathaushalt auf verschiedenen Bodenarten, bei verschiedenen Phosphatzuständen und für die wichtigsten Gewächse, ausführlich verfolgt wird.

Tabelle V gibt Zahlen für die chemische Zusammensetzung des Zitronensäure- und des Milchsäure-Extraktes verschiedener Konzentration. Unterschiede in Phosphatzahlen zwischen beiden Säuren gehen ziemlich parallel mit Unterschieden in gelöstem Eisen + Aluminium. Es zeigen sich bemerkenswerte Unterschiede im Verlauf der CaO-Löslichkeit, welche sich aber nicht in den Phosphatzahlen wiederfinden lassen.