THE ABSORPTION OF PHOSPHATES AND POTASSIUM BY SOILS.

BY

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., February 23, 1905.

Sir: I have the the honor to transmit herewith the manuscript of a technical paper entitled "The Absorption of Phosphates and Potassium by Soils," and to recommend that it be published as Bulletin No. 32 of the Bureau of Soils.

Respectfully, Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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PREFACE.

It has long been known that soils possess the power of selectively absorbing to varying extents the several constituents from a mixture in solution, and that even strong salts may in this way be decomposed. For instance, potassium is generally absorbed more than chlorine when a soil is treated with a solution of potassium chloride. This has been explained in the past as resulting from a simple metathetical reaction between the potassium salt and other salts already present in the soil. This explanation is now known to be unsatisfactory, for, while other bases can be found in the resulting solution, they are not present in quantities equivalent to the potassium removed and the solution is generally acid. Moreover, precisely similar results can be obtained with other absorbent media which do not contain any bases to replace the potassium. The further fact has been established that an absorbing medium has a limited capacity for taking up any particular substance or constituent, and this capacity, or saturation limit, is generally independent of any simple molecular ratio between the absorbed substance and any component or constituent of the absorbing medium, organic substances, such as dyes, being absorbed in precisely the same way as mineral solutes.

The absorption phenomena resemble in many respects well-known solution phenomena, and there is a distribution of the substance which is being absorbed between the solid absorbing medium and the liquid medium, the resulting concentration of the latter depending upon the amount of the absorbed material in the solid. Whether or not there is a definite law governing the distribution is a matter of controversy, experimental evidence for and against being recorded in the literature. The reverse process of the leaching of a soil or solid containing an absorbed substance shows similar distribution phenomena between the solid and liquid media.

From these observations it follows that absorption is not merely the result of simple metathesis, although such a reaction may be involved in any given case. So may be involved adsorption or surface condensation, the formation of solid solutions, or the formation of new molecular species, it being often difficult if not impossible definitely to determine the cause or causes in any given case. But however

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complex the ultimate causes of absorption, the law governing the effect itself is one of the utmost simplicity, as the following pages will show, and the reverse process of the removal of absorbed constituents by leaching appears to follow a law similar to the law for absorption. The differential equation describing the law is identical in form with the equation describing rate of solution.

An important observation indicated by this study is that when a soil containing phosphates or potassium is leached, after a certain small amount of leaching has taken place, the subsequent leachings are of practically constant small concentration, no matter how readily soluble the phosphatic or potassium compounds in the soil may be in themselves. This suggests a very close analogy to the case of a slightly soluble solid in contact with a saturated solution of itself. It is much more probable, however, that there is actually a diminution of the concentration in successive leachings, although a diminution which would not be appreciated over any range that would ever be realized either in the laboratory or in nature.

That the solubility of the absorbed substance is not a primary factor in the phenomena is shown by the action of soils toward certain dyes which can be readily leached out with alcohol but not with water, although as soluble or even more soluble in the latter as they are in the former. A very interesting case has been cited by Walker and Appleyard and by van Bemmelen, where picric acid is absorbed by silk more readily from an aqueous solution than from an alcoholic solution and not at all from a benzene solution, although picric acid is more soluble in alcohol than in either water or benzene.

It is thus made manifest that the absorptive power of the soil is to a much larger extent than any other the controlling factor in regulating the concentration of the soil solution and that, in the absence of some exceptional disturbing cause, the concentration will remain practically constant. It further appears that different soils will yield solutions of the same order of concentration. This absorption study confirms in a positive way conclusions regarding the concentration of the soil moisture, which have already been advanced in former bulletins of this Bureau, but which were reached by entirely different lines of reasoning and evidence. These conclusions, of obvious fundamental importance, furnish a new point of view for the study of the relations of plant growth to the soil and the development of a rational system of fertilizer usage which may reasonably be expected to yield results of great practical importance in soil management.

<div align="right">FRANK K. CAMERON.</div>

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THE ABSORPTION OF PHOSPHATES AND POTASSIUM BY SOILS.

INTRODUCTION.

In soils there is present the mineral débris of rock degradation and decomposition. This mineral matter forms by far the greater part of the soil, the quantity of organic material being comparatively small, although agriculturally of great significance. In the formation of soils by rock degradation numerous small fragments of the original rock persist to a greater or less extent in the soil. This has been frequently shown, notably by the recent work of Delage and Lagatu, and has been more fully discussed in Bulletin No. 30 of this Bureau. These investigations have shown that practically all the minerals originally present in rocks are found as such in arable soils. Besides these minerals from the original rocks, the soil naturally contains the products resulting from metamorphism and epigenesis, as well as the products resulting from synthetical processes within the soil itself. These minerals are all soluble to a slight degree in water, or are acted upon by water, i. e., they are hydrolized and the more soluble products of hydrolysis are found in the soil moisture.

The minerals present in the soil determine the character and, to a certain extent, the quantity of the mineral constituents in the soil solution. The quantity of the mineral constituents in the free soil moisture is, however, largely dependent on the absorptive power of the soil, as will be shown in the following pages. It has long been known that soils have the power to absorb mineral constituents in considerable quantities from solution, and it is highly probable that synthetic as well as destructive processes are taking place in the mineral species of the soil. The well-known experiments of Way, Liebig, Heiden, Knop, Rautenberg, Peters, Voelcker, King, and others have established the general fact that the arable soils show a selective absorption toward different mineral constituents. In view of the importance of this subject to a proper understanding of the chemistry of the soil and of soil solutions, a systematic study of the behavior of several soil types toward phosphate and potassium has been made. The absorption of phosphate (PO_4) and of potassium (K) has been specially studied in the light of

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its influence in maintaining the concentration of these two important plant-food constituents in the soil moisture. The rock-forming phosphatic and potassium minerals of the soil yield and apparently continue to yield a solution whose concentration approaches equilibrium between the solution and the solid. As actual equilibrium is probably never realized under such conditions, the concentration is influenced by the area of surface exposed to the action of the soil moisture during a limited period of time. This concentration appears to be constant for any given soil and is dependent on the nature of the minerals in the soil, whether they are readily acted upon by water, carbon dioxide, or other substances dissolved in the soil moisture, and on the absorptive capacity of the soil. The magnitude of the absorption and the slow rate of removal of the absorbed material from the soil make it highly probable that the concentration of the constituents of the soil moisture is largely controlled by the absorptive power of the soil. If, for instance, the concentration of the soil solution in phosphate be reduced through any cause, such as removal of phosphate by plants or influx of rain water, the tendency will be to restore the original concentration by more of the absorbed phosphate of the soil entering into the free soil moisture. If, on the other hand, the phosphate content of the soil moisture be increased above the natural concentration for that soil— as, for instance, by the application of a soluble phosphatic fertilizer or the evaporation of soil moisture—the concentration would be reduced by absorption to the original strength. This is shown in the following experiments on the absorption of phosphate, the removal of the absorbed phosphate, and the removal of the phosphate originally in the soil. The concentration of phosphate in the solution is maintained with much persistence, although only a fractional part of the absorbed phosphate has been removed, thus indicating that while the absorbed phosphate is apparently rendered insoluble, it is nevertheless slowly but constantly going into the soil moisture. The results with potassium, though not so complete, appear to be similar in all respects to those obtained with the phosphate.

DESCRIPTION OF THE SOILS.

A preliminary series of absorption experiments was made with fourteen soils. They were so selected as to include types having the texture of a clay, a clay loam, a loam, a sandy loam, and a sand. The soils were treated with twice their weight of a sodium phosphate (Na_2HPO_4) solution containing 100 parts PO_4 per million, this being equivalent to an application of 200 parts PO_4 per million parts of the soil. After standing several days with occasional shaking, the supernatant liquid was filtered through a Pasteur-Chamberland filter and the concentration of phosphate in the filtrate determined colorimetrically. The results are given in Table I.

TABLE I.—*Absorption of phosphate by different soils from a solution of disodium phosphate containing 100 parts PO_4 per million.*

Soil.	Quantity PO_4 in filtrate.	Quantity PO_4 absorbed by soil.	Soil.	Quantity PO_4 in filtrate.	Quantity PO_4 absorbed by soil.
	Parts per million.	*Parts per million.*		*Parts per million.*	*Parts per million.*
Cecil clay.....................	5	190	Leonardtown loam	28	144
Susquehanna clay............	9	182	Memphis silt loam...........	13	174
Brightwood clay	10	180	Sassafras sandy loam	15	170
Penn loam	5	190	Cecil sandy loam	35	130
Hagerstown loam	7	186	Podunk fine sandy loam.....	25	150
Elkton clay	10	180	Norfolk fine sand............	30	140
Sea island cotton soil.........	16	168	Sandhill	60	80

It is at once apparent that all these soils have a marked power to absorb the phosphate from the solution, reducing the concentration from 100 to as low a concentration as 5 parts per million. On the whole a second treatment gave results that were much the same as in the first, and it became obvious that the absorptive effect of the soil was not reduced by the phosphate already absorbed, in such quantities as resulted from the first treatment. On the other hand, the different soils did show considerable variations in respect to the concentration of the phosphate remaining in solution. That the absorption is also quite rapid is shown by the following experiment, in which 100-gram portions of the soils were treated with 500 c. c. of a monocalcium phosphate $(CaH_4(PO_4)_2)$ solution containing 100 parts per million PO_4. This is equivalent to an application of 500 parts per million PO_4 to the soil. At the end of the respective periods of time given in Table II the solutions were filtered as rapidly as possible. The clay mixtures required some minutes to filter, and this soil was therefore in contact with the solution longer than the periods indicated. It will be noticed that in the case of the clay soil the absorption was very rapid, 400 parts per million being absorbed by the soil in the three-minute period out of the total absorption of 445 parts per million in the twenty-four hour period. In the case of the fine sandy soil the absorption was not so rapid, only 235 parts per million being absorbed in the shorter period out of the 370 parts per million absorbed in the longer period.

TABLE II.—*Absorption of phosphate from a solution of monocalcium phosphate containing 100 parts PO_4 per million.*

Time.	Clay soil.		Fine sandy soil.	
	Quantity PO_4 in filtrate.	Quantity PO_4 absorbed by soil.	Quantity PO_4 in filtrate.	Quantity PO_4 absorbed by soil.
	Parts per million.	*Parts per million.*	*Parts per million.*	*Parts per million.*
3 minutes......................................	20	400	53	235
40 minutes.....................................	18	410	49	255
1 hour	17	415	48	260
2 hours..	13	435	37	315
4 hours..	12	440	33	335
24 hours.......................................	11	445	26	370

Four of the above soils were taken for a more thorough study, the selection being based on texture as well as on differences in absorptive power, as shown in the above experiment. The soils chosen were the Cecil clay, the Penn loam, the Podunk fine sandy loam, and the Norfolk fine sand.

The following tables show the results of the mechanical and chemical analyses of the samples of these soils used:

TABLE III.—*Mechanical analyses of the soils used in the absorption of phosphates.*

Soil.	Fine gravel, coarse sand, medium sand, 2.0 to 0.25 mm.	Fine sand, very fine sand, 0.25 to 0.05 mm.	Silt, 0.05 to 0.005 mm.	Clay, 0.005 to 0 mm.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Cecil clay..	20.3	26.3	22.3	30.5
Penn loam..	11.0	12.8	44.6	31.4
Podunk fine sandy loam.............................	2.9	66.5	23.1	6.8
Norfolk fine sand......................................	10.8	69.0	13.2	6.7

TABLE IV.—*Chemical analyses of the soils used in the absorption of phosphates, by digestion with hydrochloric acid of sp. gr. 1.115.*

Soil.	K_2O.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	P_2O_5.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Cecil clay..................................	0.19	0.34	0.29	18.51	3.28	0.13
Penn loam..................................	.61	.32	1.16	11.56	2.34	.11
Podunk fine sandy loam.................	.21	1.37	.85	5.32	1.21	.47
Norfolk fine sand........................	.22	.28	.23	2.51	1.19	.08

The Cecil clay came from Statesville, N. C., and is described[a] as a heavy red soil from 2 to 7 inches in depth, with an average depth of 5 inches, resting on a subsoil of stiff, tenacious red clay. It is a residual soil formed by the long-continued process of decomposition from a number of rock types distinct in their physical and mineralogical characters. The soil has been derived from nearly all the rocks occurring in this section, mainly hornblende gneiss, micaceous schists, coarse-grained granites, and to a less extent soapstone or steatite. Many of these rocks differ quite widely, yet so completely have they been weathered that they give rise to the same distinctive red clays. The change from the soil to the unweathered rock is nearly always gradual, and frequently it is difficult to mark the dividing line between the two. Often the rocks have decayed so thoroughly that it is difficult to determine their original composition. Again the structure of the rocks may be preserved, but on digging into what seems to be comparatively sound rock the material crumbles between the fingers, showing how completely decomposition has taken place.

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[a] Soil Survey of the Statesville Area, North Carolina. Field Operations of the Bureau of Soils, 1901.

The Penn loam came from Leesburg, Va., and is described[a] as consisting of from 8 to 12 inches of dark, Indian-red loam, underlain by a heavier loam of the same color. It is residual in origin, being derived from the weathering of the Triassic red sandstone. This rock is composed of grains of sand coated with films of ferruginous clay. In the vicinity of Leesburg, Va., and northward, some wedges, or lenses, of limestone conglomerate are intercalated into the formation, thinning out very gradually into a fine point. Where this limestone conglomerate occurs in considerable quantities with the red sandstone it gives rise to the type of soil known as Penn clay. Owing to the very irregular and peculiar contact of the two formations the boundaries between the Penn clay and the Penn loam are not sharply marked, but consists of a zone of slow gradation of one type into the other.

The sample of soil used in these experiments is shown by its mechanical analysis to be one of these gradations, having rather the texture of a clay loam.

The Podunk fine sandy loam came from South Windsor, Conn., and is described[b] as consisting of 12 inches of friable, dark-brown fine sandy loam, underlain with a yellow or brownish fine sandy loam. The material composing this soil originated by deposition in deeper lake waters, but it has been largely rewashed and redeposited by later stream action, and much of it lies within the flood plain of the rivers along which it occurs.

The Norfolk fine sand came from Upper Marlboro, Md., and is described[c] as a light-brown or yellow loamy fine sand having a depth of about 8 inches.

These four soils—the Cecil clay, the Penn loam, the Podunk fine sandy loam, and the Norfolk fine sand—were subjected to a thorough study, both as regards the absorption of phosphate and the removal of the absorbed phosphate by water. This was accomplished by passing the solution, or water, continuously through the soil contained in a filter especially devised for this purpose. The rate of flow of the liquid through the soil was entirely under control.

DESCRIPTION OF THE APPARATUS.

The apparatus used is shown in figure 1. The short filter tube A is made by cutting off the lower part of a Pasteur-Chamberland filter tube and plugging the open end with a rubber stopper. The object in

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[a] Soil Survey of Leesburg Area, Virginia. Field Operations of the Bureau of Soils, 1903.

[b] Soil Survey of the Connecticut Valley. Field Operations of the Bureau of Soils, 1899.

[c] Soil Survey of Prince George County, Md. Field Operations of the Bureau of Soils, 1901.

cutting down the filter tube is twofold, first, to decrease the filtering surface so as to make it possible thoroughly to control the flow by the device to be described presently, and second, to have the filtering surface as nearly as practicable at the bottom of the chamber so that the solution must pass through the entire soil column. This might be more effectually accomplished by the use of filtering disks, but no filtering material could be found which was suitable for this work. The filter tube was cut so as to leave about 2 cm. of the tube projecting above the rubber stopper, which holds it firmly in position in the metallic tube B serving as the receptacle for the soil. The metallic tube is closed at the upper end with a two-hole rubber stopper provided with two glass tubes. One of these tubes is about 6 feet in length, the end being connected with a funnel. If a greater pressure than 6 feet is necessary for forcing the liquid through a soil, a piece of tubing is readily added and any desired pressure obtained. A height of more than 6 feet was, however, necessary in only a single case in the course of these experiments. The shorter tube provided with a rubber tube and pinchcock serves to let the entrapped air out of the metal tube when starting the apparatus.

The rate of flow of the liquid through the soil is controlled by means of the glass spiral siphon C, constructed of very thin walled capillary tubing, the tubing being of such a length that the friction of the liquid in passing through it gives the desired rate of flow. The spiral was suspended in the solution to be used, contained in a beaker of such large diameter that the level of the liquid was not materially changed overnight by the flow through the siphon. It was found that the rate of flow was not sensibly affected by slight changes in the height of the liquid in the reservoir. Devices like the Mariotte constant-level bottle were also tried, but the rate required was so slow that no satisfactory flow of liquid could be maintained. The length of the spiral was adjusted so that about 50 c. c. passed in twenty-four hours.

Fig. 1.—Apparatus used in the absorption experiments.

The apparatus may be charged by putting about 50 c. c. of water or of the solution to be used into the percolating tube and then adding the finely powdered soil in such a way as to prevent trapping of air, or the soil may be made into a thin paste with the solution and this poured into the tube. The latter is then set in a vertical position in a stand and connected with the rest of the apparatus by inserting the
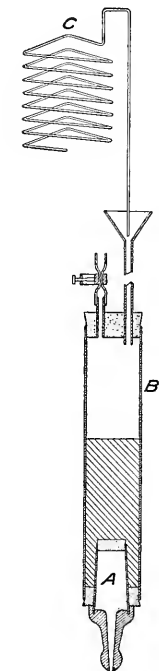
rubber stopper. The pinchcock is opened and some of the liquid poured into the funnel until the metal tube is full. The pinchcock is then closed and the glass tube filled with liquid by pouring into the funnel. The constant-dropping spiral is then put in position, as shown in the figure, and the funnel covered to prevent evaporation. The pressure of the column of liquid in the tube forces the solution through the soil and through the filter, A, and if the rate of filtration is greater than the rate with which the liquid is supplied by the constant-dropping spiral the height of liquid in the glass tube will decrease until the pressure of the column is sufficient to force the liquid through the filter at the same rate as it is supplied by the dropping siphon. As the column of liquid becomes shorter, the pressure is diminished and the filtration is less rapid, until finally the rate is exactly that of the dropping spiral. If the filtration should tend to become slower than this rate, the column of liquid in the tube will rise and the consequent greater pressure will be sufficient to keep the rate of filtration constant and identical with that of the dropping spiral. The apparatus becomes, therefore, perfectly automatic as far as the rate of flow of the liquid is concerned. It is of course necessary that the filter be sufficiently close grained, a condition easily obtained with the filters mentioned, and that the filtering surface be sufficiently small so as not to filter faster than the desired rate without the application of some pressure.

REMOVAL OF PHOSPHATE BY WATER.

A study of the absorption by soils of phosphate from aqueous solutions and the removal of the absorbed phosphate by water requires a definite knowledge as to the behavior of the phosphate originally in the soils toward the solvent action of water under the identical conditions used in the absorption experiments. To ascertain this the soils selected for the investigation were treated with distilled water, and determinations made of the phosphate in the various fractions of percolate.

For this purpose the apparatus already described was used and the tubes were charged with 100 grams of soil. As already mentioned, the soils studied were a clay, a clay loam, a fine sandy loam, and a fine sand. The soils had been collected several months previously and were air dry. Pure distilled water was allowed to flow through the soil at the rate of 50 c. c. in twenty-four hours. The percolate was collected in fractions and the phosphate concentrations determined by means of the colorimetric method described in a former bulletin.[a] The results obtained with the clay soil are given in Table V.

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[a] Bul. No. 31, Bureau of Soils, U. S. Dept. of Agr., 1905, p. 42.

TABLE V.—*Removal of phosphate from a clay soil by water.*

Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.
Cubic centimeters.	*Parts per million.*	*Parts per million.*	*Cubic centimeters.*	*Parts per million.*	*Parts per million.*	*Cubic centimeters.*	*Parts per million.*	*Parts per million.*
40	26	10	360	7	35	690	7	55
130	8	18	540	6	45	740	5	57
170	8	21	590	6	48	790	7	61
260	8	28	640	6	51	850	7	64

In the first column is given the total number of cubic centimeters of the solution which have passed through the soil, the concentrations of the separate fractions in phosphate being given in the second column. In the third column are the figures for the total quantity removed by the water, the results being expressed in terms of parts PO_4 per million parts of the soil. It will be noticed that after the first portion, which is considerably stronger than the others, has passed the solution has practically a constant concentration in phosphate.

The results for the clay loam are given in Table VI. In this case the concentration is likewise greatest in the first portion, diminishing with succeeding portions, although the drop is not so abrupt as with the clay soil, until again a constant concentration of solution is obtained.

TABLE VI.—*Removal of phosphate from a clay loam by water.*

Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.
Cubic centimeters.	*Parts per million.*	*Parts per million.*	*Cubic centimeters.*	*Parts per million.*	*Parts per million.*	*Cubic centimeters.*	*Parts per million.*	*Parts per million.*
30	19	6	250	6	28	510	6	45
80	17	15	360	6	35	550	6	47
140	10	20	410	6	38			
190	10	25	460	7	41			

In Table VII are given the results obtained with the fine sandy loam. Here the first result is lower than the succeeding ones, but likewise there is the same tendency to yield a solution of constant concentration in phosphate, although this is considerably higher than in the solutions obtained from the other soils. This is perhaps due to the greater rate of solubility of the phosphatic mineral constituents[a] of the Podunk fine sandy loam used in this experiment as well as to the lower absorptive capacity of this soil. The other minerals of this soil are likewise quite soluble, and a solution quite high in total salts, comparatively speaking, is obtained.

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[a] Cameron and Hurst [Jour. Amer. Chem. Soc., **26**, 885 (1904)] have shown that for short-time intervals the rate of solubility of phosphoric acid from slightly soluble phosphates is conditioned by the ratio between the solid and the water.

TABLE VII.—*Removal of phosphate from a fine sandy loam by water.*

Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.
Cubic centimeters.	*Parts per million.*	*Parts per million.*	*Cubic centimeters.*	*Parts per million.*	*Parts per million.*	*Cubic centimeters.*	*Parts per million.*	*Parts per million.*
50	17	8	200	23	45	400	19	75
100	25	22	300	21	55	460	19	85
150	25	34	350	18	64	510	21	96

The results obtained with the fine sandy soil are given in Table VIII and are similar to those already given.

TABLE VIII.—*Removal of phosphate from a fine sandy soil by water.*

Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.	Volume of percolate.	Quantity of PO_4 in solution.	Total quantity of PO_4 extracted from soil.
C. c.	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*
60	16	9	380	5	32	580	6	45
110	12	16	430	7	36	640	6	48
180	7	21	480	6	39			
230	7	25	530	5	42			

The general tendency of the soils is to yield more concentrated fractions at the start, but soon to give a solution of nearly constant concentration in phosphate for each soil examined. The higher concentration obtained at the start is interesting, especially in the light of some of the absorption phenomena to be described further on in this bulletin. To ascribe this to the existence in the soil of more readily soluble phosphates which are quickly leached out seems not to be tenable in view of the great absorptive power of these soils for phosphate, even when introduced in exceedingly soluble forms, as has already been shown. The greater concentration in the first portions seems rather to be connected with the air-dry condition of the soils. In earlier bulletins from this Bureau [a] it has been demonstrated that oven and air dried soils yield a greater quantity of soluble salt to water than do the same soils in the moist condition. This greater concentration in phosphate in the case of the dried soils may be, at least in part, due to the lower absorptive power of the soil when used in the dry form, and will be considered later.

ABSORPTION OF PHOSPHATE FROM A SOLUTION OF MONOCALCIUM PHOSPHATE.

The phosphate used in these experiments was the monocalcium phosphate, $CaH_4(PO_4)_2$, as this is the most soluble of the phosphates of

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[a] Bureau of Soils, U. S. Dept. of Agr., Bul. 22, 1903, p. 42; Bul. 26, 1905, p. 55.

calcium and also the one occurring in superphosphate fertilizers. A solution containing 200 parts of PO_4 per million of the solution was prepared by diluting a stronger solution which had been standardized by gravimetric analysis.

In these experiments the same samples of soils used in the previous experiment with the water percolation were studied. The tubes of soil were allowed to drain thoroughly. The apparatus was then filled with this solution as already described under the water percolation. The volume of water or rather soil solution remaining in the apparatus must necessarily have been less than 50 c.c. and this volume of percolate was discarded at the beginning of the flow of solution through it. The flow was maintained at a rate of about 50 c.c. in twenty-four hours. Fractional percolates were collected and the phosphate determined colorimetrically. The results obtained with the clay soil are given in Table IX. In the first column is given the total volume of the phosphate solution which has passed through the soil, the second column giving the concentration of phosphate in the separate portions. The third column gives the amount of phosphate absorbed by the soil, expressed in parts per million. In the fourth column are given the results calculated by means of a formula derived from certain theoretical considerations which will be developed later.

It will be seen from the table that the phosphate is almost completely absorbed from the first 400 c.c. passed, the concentration having been reduced from 200 parts per million to 6 and 8 parts per million, practically the concentration yielded by the percolation of pure water through the soil. As more solution flows through the soil the concentration of phosphate in the percolate increases, rapidly at first, and then more slowly. The absorption is still going on to a considerable extent even after the passage of nearly 6 liters of the solution and a total absorption by the soil of nearly 5,000 parts per million of phosphate. The quantity absorbed by the soil as shown in the third column increases rapidly at first and then more slowly as the total amount already absorbed increases. The fourth column will be discussed presently.

TABLE IX.—*Absorption of phosphate by a clay soil from a solution of monocalcium phosphate, $CaH_4(PO_4)_2$, containing 200 parts per million PO_4.*

Volume of percolate.	Quantity PO₄ in solution.	Total quantity PO₄ absorbed by soil.		Volume of percolate.	Quantity PO₄ in solution.	Total quantity PO₄ absorbed by soil.		Volume of percolate.	Quantity PO₄ in solution.	Total quantity PO₄ absorbed by soil.	
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C.c.	P.p.m.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	P.p.m.
250	6	480	480	1,660	101	2,470	2,480	3,890	150	4,100	4,160
410	8	790	740	2,050	115	2,800	2,880	4,290	152	4,300	4,330
570	12	1,090	1,020	2,510	108	3,220	3,270	4,640	156	4,450	4,480
780	31	1,450	1,350	2,820	111	3,440	3,510	5,000	162	4,590	4,600
1,030	58	1,800	1,720	3,260	127	3,760	3,810	5,370	158	4,740	4,720
1,330	84	2,150	2,100	3,640	142	3,980	4,030	5,740	169	4,860	4,820

In Table X are found the results obtained with the clay loam. It will be noticed that here again the concentration of the first portions is very low, approximately that obtained by the action of water on the soil, and that the concentration of the percolate rises as more solution is passed through the soil, but much more rapidly than in the case of the clay soil. The concentration when about 4 liters of solution have passed through the clay loam is appreciably greater than when 6 liters of solution have passed through the clay soil. The quantity absorbed by the clay loam is considerably less than by the clay soil when any given volume of solution has passed through the soil. The column giving the quantities absorbed by the clay loam is not materially different from that in the table for the clay soil, except in the quantities absorbed. This will be discussed later with the results in the last column.

TABLE X.—*Absorption of phosphate by a clay loam from a solution of monocalcium phosphate, $CaH_4(PO_4)_2$, containing 200 parts per million PO_4.*

Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.	
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.
110	6	220	200	1,420	138	1,830	1,810	3,410	167	2,720	2,720
220	5	420	390	1,690	137	2,000	2,000	3,700	176	2,790	2,780
360	38	650	610	1,890	159	2,080	2,130	4,050	187	2,830	2,850
590	50	990	940	2,170	155	2,210	2,280	4,340	189	2,860	2,900
730	47	1,200	1,120	2,470	150	2,360	2,420	4,570	178	2,920	2,910
940	78	1,460	1,370	2,800	148	2,530	2,550				
1,110	95	1,640	1,550	3,150	170	2,630	2,650				

In Table XI will be found the results obtained with the fine sandy loam. These are very similar in character to those for the soils already given, the concentration of the first fraction being again approximately that of the solution obtained from the soil by percolation with pure water. The total amount absorbed by the soil is, moreover, less throughout than that absorbed by either the clay loam or clay soil.

TABLE XI.—*Absorption of phosphate by a fine sandy loam from a solution of monocalcium phosphate, $CaH_4(PO_4)_2$, containing 200 parts per million PO_4.*

Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.	
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.
150	22	260	290	1,270	127	1,660	1,650	3,000	156	2,460	2,450
280	27	500	500	1,450	146	1,750	1,780	3,300	185	2,500	2,510
430	31	740	740	1,660	135	1,890	1,920	3,540	190	2,530	2,560
640	55	1,040	1,010	1,970	157	2,020	2,080	3,860	177	2,600	2,610
840	64	1,320	1,250	2,340	167	2,140	2,250	4,150	185	2,640	2,640
1,040	115	1,490	1,450	2,710	149	2,330	2,370	4,390	182	2,690	2,670

In Table XII are given the results obtained with the fine sandy soil. The absorptive power of this soil is considerably less than that of the soils already considered, as is shown by the third column of figures and also by the relatively higher concentrations in the phosphate solutions throughout. It will be noticed also that this lower absorptive power of the soil is shown by the fact that the concentration of the first fractions is higher than the concentration obtained by percolating water through the soil, while with the other soils they were approximately the same.

TABLE XII.—*Absorption of phosphate by a fine sandy soil from a solution of monocalcium phosphate, $CaH_4(PO_4)_2$, containing 200 parts per million PO_4.*

| Volume of percolate. | Quantity PO4 in solution. | Total quantity PO4 absorbed by soil. | | Volume of percolate. | Quantity PO4 in solution. | Total quantity PO4 absorbed by soil. | | Volume of percolate. | Quantity PO4 in solution. | Total quantity PO4 absorbed by soil. | |
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C.c.	P.p.m.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	P.p.m.
140	20	250	210	1,150	152	1,210	1,260	2,750	159	2,050	2,060
270	19	480	400	1,340	141	1,320	1,400	3,090	148	2,230	2,150
380	39	660	530	1,560	142	1,440	1,540	3,330	174	2,290	2,210
540	82	850	700	1,800	159	1,540	1,660	3,620	191	2,320	2,270
670	121	950	850	1,980	122	1,690	1,760	3,850	192	2,340	2,310
810	129	1,050	980	2,210	143	1,820	1,870	4,040	191	2,350	2,340
950	156	1,120	1,100	2,460	155	1,930	1,960				

REMOVAL OF ABSORBED PHOSPHATE BY WATER.

At the conclusion of the absorption experiments described in the preceding section the tubes with the soils were allowed to drain thoroughly, and then the apparatus was filled with distilled water in the manner already described. The flow of water was again at the rate of about 50 c. c. in twenty-four hours, the percolate being collected in fractions and the concentration of phosphate determined colorimetrically as before. The results obtained with the clay soil are given in Table XIII. The first column gives the volume of solution which has passed through the soil and the second the concentrations of the separate fractions as before. At the head of the third column is given the total quantity of phosphate absorbed by the soil in the previous experiment, and following this are the amounts of absorbed phosphate not washed out.

TABLE XIII.—*Removal of absorbed phosphate from a clay soil by water.*

Volume of percolate.	Quantity PO4 in solution.	Total quantity PO4 remaining in soil.	Volume of percolate.	Quantity PO4 in solution.	Total quantity PO4 remaining in soil.	Volume of percolate.	Quantity PO4 in solution.	Total quantity PO4 remaining in soil.	Volume of percolate.	Quantity PO4 in solution.	Total quantity PO4 remaining in soil.
C.c.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.
......	......	4,860	730	36	4,410	2,280	20	4,050	4,450	8	3,760
100	127	4,730	910	32	4,350	2,590	19	3,990	5,030	7	3,720
230	85	4,630	1,140	27	4,290	2,970	16	3,980	5,450	8	3,690
440	55	4,510	1,330	21	4,250	3,370	16	3,870	5,870	7	3,660
580	41	4,450	1,750	21	4,160	3,870	11	3,810	6,300	7	3,630

It will be noticed that the concentration of the first fractions is very high. The concentration in phosphate decreases rapidly at first and then very slowly, until at about 4 liters the concentration of the solution has become constant and is practically the same as that found at the beginning of the absorption and that of the percolate from the original soil, although the quantity of absorbed phosphate still remaining in the soil is nearly 3,800 parts per million, or approximately 75 per cent of the total phosphate absorbed. The results with the clay loam, given in Table XIV, show a similar tendency. The high concentration in phosphate in the first portions gradually gives place to lower concentrations, until at about 5 liters the concentration reached is that of the solution obtained at the start of the absorption or by percolating water through the original soil. The amount of absorbed phosphate still in the soil is, however, considerable at this point, being about 1,900 parts per million, or approximately 65 per cent of the total phosphate absorbed.

TABLE XIV.—*Removal of absorbed phosphate from a clay loam by water.*

Volume of percolate.	Quantity PO₄ in solution.	Total quantity PO₄ remaining in soil.	Volume of percolate.	Quantity PO₄ in solution.	Total quantity PO₄ remaining in soil.	Volume of percolate.	Quantity PO₄ in solution.	Total quantity PO₄ remaining in soil.	Volume of percolate.	Quantity PO₄ in solution.	Total quantity PO₄ remaining in soil.
$C.c.$	$P.p.m.$	$P.p.m.$	$C.c.$	$P.p.m.$	$P.p.m.$	$C.c.$	$P.p.m.$	$P.p.m.$	$C.c.$	$P.p.m.$	$P.p.m.$
....	....	2,920	1,030	23	2,500	2,460	17	2,270	4,530	11	1,980
90	89	2,840	1,250	17	2,460	2,770	17	2,210	5,100	8	1,940
180	77	2,760	1,460	17	2,420	3,080	13	2,180	5,690	7	1,900
400	41	2,670	1,700	16	2,390	3,400	16	2,120	6,270	7	1,860
630	36	2,590	1,900	15	2,360	3,730	15	2,070	6,830	6	1,820
830	25	2,540	2,200	14	2,310	3,970	14	2,040	7,340	6	1,790

The results obtained with the fine sandy loam are given in Table XV. A concentration of phosphate in the solution approximately equal to that of the first fraction in the absorption experiments, or to that of the solution obtained by percolating water through the original soil, is found to be reached when about 3 liters of percolate have been obtained. The absorbed phosphate still remaining in the soil at this point is about 1,600 parts per million, or about 60 per cent of the total quantity absorbed. The concentration of the solution in phosphate decreases, however, until it falls considerably below that of the solutions obtained by percolating water through the original soil, although there is present a much larger amount of phosphate in the soil at this stage than there was in the original soil.

TABLE XV.—*Removal of absorbed phosphate from a fine sandy loam by water.*

Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.	Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.	Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.	Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.
C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.
......	......	2,690	1,030	34	2,040	2,320	21	1,720	4,600	12	1,300
120	124	2,540	1,240	30	1,980	2,820	23	1,600	5,180	11	1,240
250	87	2,430	1,470	28	1,910	3,140	23	1,530	5,720	10	1,190
380	76	2,330	1,690	26	1,860	3,490	22	1,450	6,140	11	1,140
610	56	2,200	1,890	23	1,810	3,890	15	1,390	6,570	10	1,100
820	42	2,110	2,120	22	1,760	4,290	13	1,340			

It has been pointed out already that the Podunk fine sandy loam used in these experiments contained minerals which were acted upon by water to a very considerable extent. The percolation of over 40 times its weight of the calcium phosphate solution, containing 42 parts per million Ca in addition to the 200 parts per million PO$_4$, together with the subsequent washing with over 60 times its weight of water, has produced chemical changes in the soil itself, so that we have no longer the identical soil started with. In fact, this must be the conclusion reached from the figures given above, so far as the removal of the phosphate from the soil is concerned. In Table XVI are found the results for the fine sandy soil.

TABLE XVI.—*Removal of absorbed phosphate from a fine sandy soil by water.*

Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.	Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.	Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.	Volume of percolate.	Quantity PO$_4$ in solution.	Total quantity PO$_4$ remaining in soil.
C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.
......	......	2,350	1,060	19	1,930	2,400	10	1,760	4,610	7	1,590
110	150	2,190	1,270	17	1,890	2,680	9	1,740	5,090	7	1,550
240	51	2,120	1,490	13	1,860	2,940	8	1,710	5,670	5	1,530
430	31	2,060	1,740	13	1,830	3,200	9	1,690	6,230	6	1,490
620	24	2,020	1,950	12	1,810	3,540	7	1,670	6,660	6	1,470
840	21	1,970	2,180	11	1,780	4,100	8	1,620	7,080	5	1,450

The concentration of the phosphate in the fractions of percolate decreases rapidly at first and then very slowly, approaching a uniform concentration toward the end, which is considerably lower than that of the first fraction obtained in the absorption experiment. It is approximately the concentration obtained from the original soil by passing pure water through it, although the amount of phosphate present in the soil is considerably greater.

GRAPHICAL REPRESENTATION AND DISCUSSION OF THE RESULTS OBTAINED WITH MONOCALCIUM PHOSPHATE.

The results obtained in the foregoing experiments on the absorption of phosphate from a solution of monocalcium phosphate, together with those obtained in removing the absorbed phosphate, are shown graphically in the following figures. In figure 2 are shown the results expressed in terms of the solutions. The abscissas represent the liters of solution or of water which have been passed through the 100 grams of soil in the percolating tube. The ordinates give the concentration of the percolate in phosphate. The upper boundary line of the figure represents the strength of the solution before passing through the soil; the break in each of the curves gives the point where the 200 parts per million solution was replaced by distilled water and the washing out of the absorbed phosphate was begun. The intersection of each of the curves on the axis of ordinates shows the concentration of phosphate solution obtained by percolating water through the original soil. The curves in this figure are smoothed curves; the experimental points are not given in the diagram, since the large number and intermingling of the points would be confusing, as can be seen by examining the tables. The curves, however, represent very well the general facts brought out by the figures in the tables. It will be noticed that the absorption of phosphate from the solution by the soil is considerable for approximately the first 300 c. c. of the solution passed, and that the concentration of the solution is practically reduced to that of the soil extract obtained from the original soil. After this the curves rise with increasing volume of solution passed, rapidly in the case of the sandy soil and much more slowly in the case of the clay soil. All the curves approach the line representing the concentration of the original solution, namely, 200 parts per million, apparently as an asymptote. The curves for the removal of the absorbed phosphate show a very decided drop at the start and then rapidly tend to become horizontal when concentrations have been reached approximating those of the water extracts of the original soils or those of the first few fractions of percolate in the absorption experiments. This is shown by comparing the extremes of the curves. It is, moreover, significant that the soils, after this absorption treatment, yield solutions which are much closer together in concentration of phosphate than did the original soils, although the quantities of phosphate in the soils are in all cases greater than those originally present. The concentrations at the ends of the curves are practically identical in the case of the fine sandy soil, clay loam, and clay soil studied. In the case of the fine sandy loam the concentration of the aqueous extract of the original soil is somewhat greater than the concentration of the last percolate,

although the soil actually contains more phosphates than it did originally.

In figure 3 are shown the results on the basis of the soil itself, the abscissas being the liters of solution passed as before and the ordinates the parts of phosphate per million parts of soil. The experimental points as found in the tables are indicated in the figure by specific signs. It is at once apparent that the absorption curves of the differ-
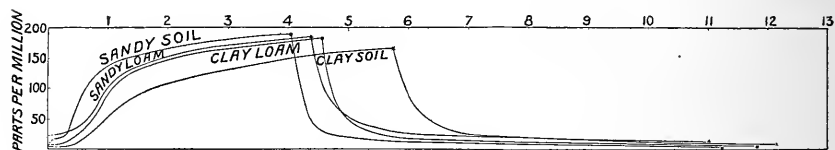

Fig. 2.—Solution curves. Absorption of phosphate by soils from a solution of monocalcium phosphate and the removal of the absorbed phosphate by water.
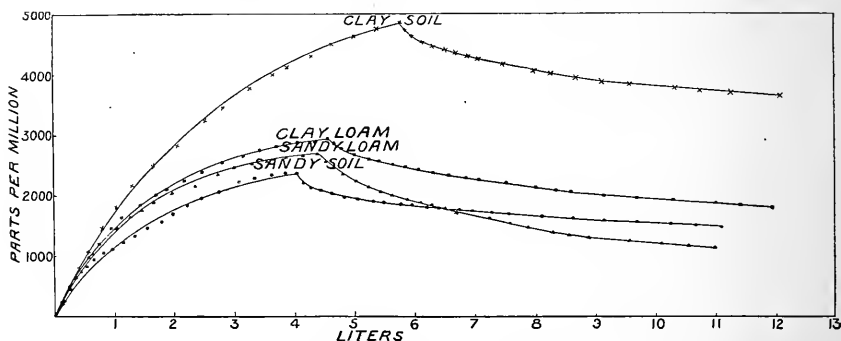

Fig. 3.—Soil curves. Absorption of phosphate by soils from a solution of monocalcium phosphate and the removal of the absorbed phosphate by water.

ent soils are quite similar in character, although these soils differ in the amount of the phosphates absorbed at any given abscissa. The curve for the sandy soil indicates a rapid approach to a horizontal position, that is, a condition of saturation for phosphate, at about 2,400 parts per million, whereas the curve for the clay soil at about twice the height is still showing a decided tendency to rise. The curves for the removal of the absorbed phosphate drop rapidly at first and then run smoothly and gradually downward. The removal curve for the sandy loam has a steeper slope than the others, which fact is of course also shown by the higher concentration of the phosphate solution, as appears from figure 2. A comparison of the two figures shows also very strikingly that with all the soils studied a solution of low phosphate content, approximately of the strength of the extract obtained from the original soil, is obtained when only a fractional part of the absorbed phosphate has been removed.

These graphical representations of the absorption results indicate, as has already been pointed out, that the soils are approaching a saturation for phosphate under the conditions of the experiment, as is shown by the fact that each curve is evidently approaching a horizontal asymptote. It has been found that these absorption phenomena are quite accurately represented by an expression of the same form as monomolecular reaction velocities, rate of solution, and other analogous processes. Lagergren[a] has already shown that the rate of adsorption of several organic acids by charcoal, in respect to time, behaves like a monomolecular reaction.

If we represent the maximum quantity that the soil can take up from the 200 parts per million solution, that is, the ordinate of the asymptote just mentioned, and let y equal the parts per million PO_4 it has taken up when the volume v has passed through the soil, the simplest assumption that can be made is that the quantity absorbed from a unit volume of solution as it passes through the soil is proportional to the amount the soil can still take up. This is represented by the following differential equation:

$$\frac{dy}{dv} = K(A-y).$$

Integrating between limits

$$\int_0^y \frac{dy}{A-y} = K \int_0^v dv$$

we get

$$\log (A-y) - \log A = -Kv,$$

or

$$\log (A-y) = \log A - Kv.$$

Since $\log A$ and K are constants to be found from the observations, Briggsian instead of Naperian logarithms may be used in the calculations. This will merely change the values of K and $\log A$ in the same ratio.

The simplest way to test the applicability of the equation appears to be (1) to determine A by inspection of the curve obtained by plotting the experimental data; (2) to make a table of $\log (A-y)$; (3) to make a plot using v as abscissa and $\log (A-y)$ as ordinate. It will

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[a] Bihang till K. Sv. Vet.-Akad. Handl., **24**, Afd. II, No. 5 (1898).

be noticed that the above logarithmic equation is that of a straight line. The plot will therefore be a straight line if the correct value for A has been chosen. The intercept on the axis of ordinates is log A and the slope of the line gives the constant K.

The absorption results for all of the soils studied have been tested in this way, and it has been found that a fair agreement with the formula is obtained when the following constants are used:

Soil.	A.	log A.	K.
Clay soil...................	5,500	3.740	0.000158
Clay loam	3,100	3.491	.000267
Sandy loam	2,800	3.447	.000299
Fine sandy soil............	2,600	3.413	.000247

The results obtained by using these values in calculating the parts per million PO_4 absorbed by the soil for any given volume of the solution which has percolated through it are given in the fourth columns of the tables for the respective soils. In figure 3 the absorption curves are drawn through the calculated points, and the experimental points are indicated by the specific signs. The plots show, therefore, how well the calculated and the experimental results agree. These are given in the third and fourth columns, respectively, of the absorption tables.

Apparently the removal curves are likewise represented by a similar formula when the first few points are left out of consideration. This disagreement for the first few points may be due to the fact that a part of the strong phosphate solution remained in the soil when the washing process was begun. The equation for the removal of phosphates from the soil may be written as follows:

$$\frac{dy}{dv} = K\,(y - B)$$

where B is the ordinate corresponding to the asymptote of the removal curve—that is, the amount of phosphate which has apparently become permanently insoluble so far as any reasonable amount of solvent passing through it is concerned. The calculated results obtained with this equation bring out no information not given by the plotted curves, and are therefore omitted.

ABSORPTION OF PHOSPHATE FROM A SOLUTION OF DISODIUM PHOSPHATE AND REMOVAL OF THE ABSORBED PHOSPHATE BY WATER.

In the following experiments a solution of sodium phosphate was used instead of the monocalcium phosphate of the previous experiments. The solution used contained 200 parts of PO_4 per million of the solution and was prepared by diluting a strong solution which had

been standardized by gravimetric analysis.   The same clay, clay loam, fine sandy loam, and fine sand were used as in the experiments with calcium phosphate.   The apparatus was charged by putting some of the solution into the percolating tube and then adding the dry soil. The tube was then completely filled with solution in the manner already described, and all other operations were exactly the same as in the preceding experiments.   The absorption was not carried so far as in the experiments with the calcium phosphate.

TABLE XVII.—*Absorption of phosphate by a clay soil from a solution of sodium phosphate, Na_2HPO_4, containing 200 parts per million PO_4.*

Volume of perco-late.	Quantity PO_4 in so-lution.	Total quantity PO_4 absorbed by soil.		Volume of perco-late.	Quantity PO_4 in so-lution.	Total quantity PO_4 absorbed by soil.	
		Ob-served.	Calcu-lated.			Ob-served.	Calcu-lated.
C. c.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
190	154	90	....	610	12	890	900
220	23	150	150	740	24	1,110	1,110
320	8	330	330	850	42	1,280	1,280
410	5	510	510	900	48	1,360	1,370
520	8	710	710	970	61	1,470	1,480

In Table XVII are given the absorption results with the clay soil. As before, the fourth column gives the amount calculated by a formula to be discussed presently.   It is at once apparent from the second column, giving the concentration in phosphate of the separate percolates, that the results differ from those where the wet soil was treated with the solution of monocalcium phosphate.   The concentration in phosphate, instead of being low at the very start and then gradually rising, is in this case quite high at first, rapidly drops down to a very low concentration, and then rises gradually.   This high concentration at the start may be due in part to the more rapid movement of the liquid through the soil in the beginning, while the rate of flow is becoming adjusted, but the less absorptive power of the soil when brought in the dry form into contact with the solution is probably a much more potent cause.

When 1,470 parts PO_4 per million had been absorbed by the soil, the drained soil was treated with water in the manner previously described.   The results are given in Table XVIII.

TABLE XVIII.—*Removal of absorbed phosphate from a clay soil by water.*

Volume of perco-late.	Quantity PO_4 in so-lution.	Total quantity PO_4 re-maining in soil.	Volume of perco-late.	Quantity PO_4 in so-lution.	Total quantity PO_4 re-maining in soil.	Volume of perco-late.	Quantity PO_4 in so-lution.	Total quantity PO_4 re-maining in soil.
C. c.	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*
....	....	1,470	500	14	1,340	1,140	8	1,290
100	47	1,420	60'	9	1,330	1,330	11	1,270
220	31	1,380	720	7	1,320	1,500	9	1,250
320	15	1,360	870	7	1,310	1,650	11	1,240
410	15	1,350	990	9	1,300			

The second column in the table indicates very strikingly the similarity in the removal of the absorbed phosphate from this soil and from the same soil in the preceding series, in that the solutions rapidly run down to a practically constant concentration which is comparable with that obtained from the original soil by percolation with water. As in the preceding series, the amount of absorbed phosphate remaining in the soil when this constant concentration of the soil solution is reached is still large.

In Table XIX are given the absorption results obtained with the clay loam.

TABLE XIX.—*Absorption of phosphate by a clay loam from a solution of sodium phosphate, Na_2HPO_4, containing 200 parts per million PO_4.*

Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.	
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C. c.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
60	127	40	....	360	5	620	640	770	71	1,180	1,170
100	19	120	120	460	19	760	760	810	86	1,240	1,230
150	8	220	220	550	32	910	920				
260	4	430	430	660	77	1,050	1,050				

These results are seen to be very similar to those obtained with the clay, the concentration of the solution rapidly decreasing to a very low value, and then gradually rising. The passage of the solution was exceedingly slow in this case and a considerable length of tubing had to be added to the apparatus in order to secure the necessary pressure for forcing the solution through the soil. For this reason the experiment was stopped when only about 1,200 parts per million PO_4 had been absorbed by the soil. The percolate was far from showing a saturated condition for the soil. An attempt was nevertheless made to study the removal of the absorbed phosphate by water, but when approximately 600 c. c. had passed the pressure necessary for filtration became so great that the experiment could not be continued in the apparatus used. The few results obtained are given in Table XX.

TABLE XX.—*Removal of absorbed phosphate from a clay loam by water.*

Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 remaining in soil.	Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 remaining in soil.
C. c.	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*
....	....	1,240	380	54	940
90	77	1,170	490	48	910
200	75	1,090	580	46	870
300	78	1,010			

The results show the same general tendency as in the experiments already described. It will also be noticed that these results, together with those of the previous experiment, show conclusively that the washing-out process of the absorbed phosphate is essentially the same in kind, whether the soil has absorbed a large or a small amount of phosphate.

The absorption results obtained with the fine sandy loam are given in Table XXI.

TABLE XXI.—*Absorption of phosphate by a fine sandy loam from a solution of sodium phosphate, Na_2HPO_4, containing 200 parts per million PO_4.*

| Vol-ume of per-colate. | Quan-tity PO_4 in solu-tion. | Total quantity PO_4 absorbed by soil. | | Vol-ume of per-colate. | Quan-tity PO_4 in solu-tion. | Total quantity PO_4 absorbed by soil. | | Vol-ume of per-colate. | Quan-tity PO_4 in solu-tion. | Total quantity PO_4 absorbed by soil. | |
		Ob-served.	Calcu-lated.			Ob-served.	Calcu-lated.			Ob-served.	Calcu-lated.
C. c.	*P.p.m.*	*P.p.m.*	*P.p.m.*	*C. c.*	*P.p.m.*	*P.p.m.*	*P.p.m.*	*C. c.*	*P.p.m.*	*P.p.m.*	*P.p.m.*
50	175	10	....	580	101	540	520	1,320	165	890	920
280	130	170	170	680	105	640	600	1,480	174	940	960
330	48	250	240	780	143	690	680	1,700	174	1,000	1,000
380	62	310	310	940	152	770	770	1,860	176	1,030	1,020
470	72	440	410	1,090	167	810	840	1,960	195	1,040	1,030

These results are similar to those obtained with the other soils. The last results in the second column indicate that the soil is approaching a saturated condition, although only about 1,000 parts per million are absorbed. This is a much lower absorption than in the case of the monocalcium phosphate with the same soil.

Table XXII gives the results for the removal of the absorbed phosphate from this soil.

TABLE XXII.—*Removal of absorbed phosphate from a fine sandy loam by water.*

Volume of perco-late.	Quantity PO_4 in solution.	Total quantity PO_4 re-maining in soil.	Volume of perco-late.	Quantity PO_4 in solution.	Total quantity PO_4 re-maining in soil.	Volume of perco-late.	Quantity PO_4 in solution.	Total quantity PO_4 re-maining in soil.
C. c.	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*
....	....	1,040	620	23	560	1,240	13	460
130	165	820	750	20	530	1,340	15	450
290	111	650	920	16	510	1,470	15	430
400	32	610	1,010	14	490			
500	26	580	1,110	13	480			

Here again the concentration of the solution runs down rapidly, until when about 900 c. c. have passed the concentration becomes practically constant and comparable with that obtained when mono-calcium phosphate was used, although the absolute concentration is slightly higher. This shows in the case of this soil that the results with sodium phosphate differ from those with monocalcium phosphate, both as regards absorption and removal.

The absorption and removal of phosphate for the fine sandy soil are given in Tables XXIII and XXIV, respectively.

TABLE XXIII.—*Absorption of phosphate by a fine sandy soil from a solution of sodium phosphate, Na_2HPO_4, containing 200 parts per million PO_4.*

Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.		Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 absorbed by soil.	
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C.c.	P.p.m.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	P.p.m.
200	145	110	....	460	97	490	480	1,120	145	930	940
240	22	190	190	610	90	660	630	1,360	155	1,040	1,020
300	9	300	280	690	106	730	700	1,550	190	1,050	1,070
350	33	380	350	800	159	770	780	1,670	168	1,090	1,090
400	88	410	410	970	158	850	870				

TABLE XXIV.—*Removal of absorbed phosphate from a fine sandy soil by water.*

Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 remaining in soil.	Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 remaining in soil.	Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 remaining in soil.	Volume of percolate.	Quantity PO_4 in solution.	Total quantity PO_4 remaining in soil.
C.c.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.	C.c.	P.p.m.	P.p.m.
....		1,090	400	25	800	1,040	10	720	1,490	8	680
90	145	960	520	22	780	1,130	10	710	1,590	7	670
170	91	890	700	12	760	1,220	9	700	1,670	7	660
290	52	830	900	14	730	1,390	8	680			

The second column of the absorption table indicates that this soil, like the preceding one, is approaching saturation at a much lower phosphate content than in the case with the monocalcium phosphate. The removal of the absorbed phosphate is the same as in the other soils, a practically constant concentration being reached when about 1,200 c. c. have passed through the soil. This concentration is practically the same as that in the case of the monocalcium phosphate.

GRAPHICAL REPRESENTATION AND DISCUSSION OF THE RESULTS OBTAINED WITH SODIUM PHOSPHATE.

In figure 4 the results of the preceding experiments on the absorption and removal of phosphate are plotted for the soil. As before, the ordinates represent the quantity of phosphate absorbed by the soil, and the abscissas the volume of solution or of water which has been passed through the soil. The break in the curves gives the point where the phosphate solution was replaced by distilled water and the washing out of the absorbed phosphate begun.

It is at once apparent that the sandy soil and sandy loam are approaching a condition of saturation, whereas the curves for the clay loam and clay soil are still rising rapidly and the soils are obviously far from saturation for phosphate. The greater absorption of the clay

loam is, moreover, only apparent, being due entirely to the different starting points of the curves. When the starting points of the curves are made to coincide, the clay loam curve lies throughout below that of the clay soil curve, as it did in the case of the monocalcium phosphate. This will be more strikingly brought out in the application of the formula to these curves, when it will be shown that they are described by the same formula and have practically the same constants as those found to apply to the case of the monocalcium phosphate. There is, however, an actual inversion of the curves in the case of the sandy loam and fine sand, the former showing the less absorptive power in this case, whereas with the monocalcium phosphate it showed the
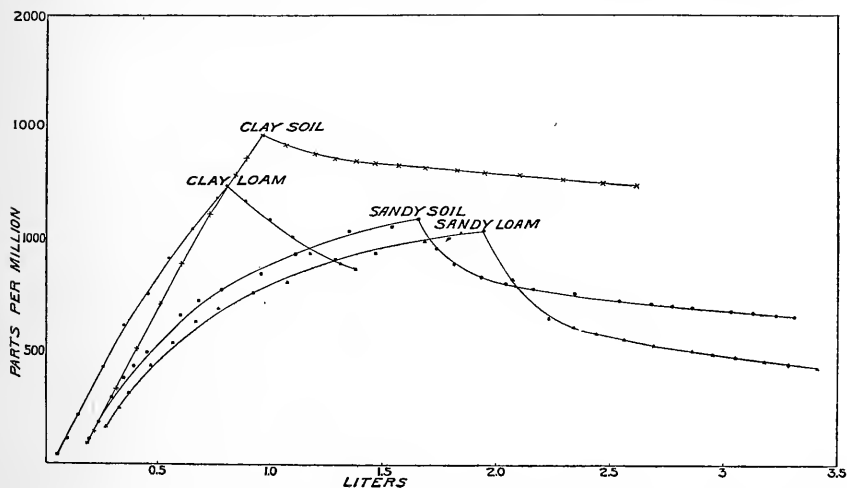

FIG. 4.—Soil curves. Absorption of phosphate by soils from a solution of disodium phosphate and the removal of the absorbed phosphate by water.

higher absorptive power. Here again the difference between the two curves is much less than it appears to be, for if the starting points of the curves were made to coincide the curves would lie much closer together. The fact remains, however, that these two soils show a relatively different absorptive power in the case of the sodium phosphate from that shown where monocalcium phosphate was used. That the specific absorptive capacity of both these soils is markedly different in the present series than in the former series will be shown presently.

The removal curves are in general the same as those in the monocalcium series already given. With the almost saturated soils the curves drop rapidly at first, but soon descend at a slow and practically uniform rate. With the less saturated soils the drop is less marked, but the results, nevertheless, clearly show that distilled water is slowly but constantly removing the absorbed phosphate, whether the soil is nearly saturated for phosphate or whether it is only partially saturated. This latter result was, of course, to be expected, since the

phosphate originally in the soils was found to be removed by distilled water at a practically constant rate.

It has been found that the same differential equation describes the absorption curves in the case of the sodium phosphate as in the case of the monocalcium phosphate. It will be observed from the figure that the curves do not go to the origin, as they did in the case of the monocalcium phosphate. This is due to the lower absorption at the very start of the experiment, either because of the lower absorptive power of the dry soil used in the present series as compared with the wet soil used in the previous series or because of the too rapid flow of the strong phosphate solution at the start before the apparatus was thoroughly regulated. Whatever may have been the cause, it is for this reason obviously necessary to modify slightly the constant $\log A$ in the equation

$$\log (A-y) = \log A - Kv$$

by substituting $\log (A-y_0)$, where y_0 is the ordinate of the point taken as the first reading, and also substituting the corresponding value of $(v-v_0)$ for v, where v_0 is the volume corresponding to the y_0 taken as the first reading. The equation then becomes:

$$\log (A-y) = \log (A-y_0) - K(v-v_0).$$

It is, of course, impossible to get any idea of the value of the specific absorptive capacity of the clay soil and the clay loam from the two curves given in the figure, as these are far from showing any tendency to approach a horizontal asymptote. A careful examination of the figures, however, shows that when allowance is made for the different starting points of the curves the results fall almost exactly on the curve for the results obtained with these same soils by using monocalcium phosphate. In other words, the clay soil and the clay loam are quite accurately described by using the same value for A as in the case of the monocalcium phosphate, together with the other constants given below:

Soil.	A.	$\log (A-y_0)$.	K.
Clay soil	5,500	3.728	0.000162
Clay loam	3,100	3.474	.000290

The results for the sandy soil and the sandy loam are likewise quite accurately described by the above equation, using the following values:

Soil.	A.	$\log (A-y_0)$.	K.
Sandy loam	1,100	2.968	0.000680
Sandy soil	1,200	3.004	.000669

The results obtained by using these values are given in the fourth column of the tables for the respective soils. In the figure the absorption curve is drawn through the calculated points, the experimental points being represented by the specific signs. The figure shows, therefore, what agreement exists between the results given in the third and fourth columns, respectively, of the absorption tables.

In the following table is given a comparison of the specific absorptive capacities for phosphate found for the four soils when sodium phosphate was used and when monocalcium phosphate was used, together with the constant K. The values of $\log A$ and $\log (A - y_0)$ may be omitted in the comparison, as they depend on the above specific absorptive capacity and the starting point of the curves.

Soil.	Monocalcium phosphate.		Sodium phosphate.	
	A.	K.	A.	K.
Clay soil	5,500	0.000158	5,500	0.000162
Clay loam	3,100	.000267	3,100	.000290
Sandy loam	2,800	.000299	1,100	.000680
Sandy soil	2,600	.000247	1,200	.000669

It is at once apparent that the absorption of phosphate by the clay soil and clay loam studied is the same for the calcium and the sodium phosphate, as is shown by the equal values for the specific absorptive capacities for phosphate, A, and the close agreement for the value of K in both cases. It is possible that the ferruginous nature of these particular soils is responsible for this similarity in the absorption of the phosphate in the two cases. With the other two soils, however, the result is quite different. The use of the sodium phosphate has changed the specific absorptive capacity of both soils markedly, and also the value of K. It seems possible, therefore, that the sodium and calcium played an important part in the changes which have taken place in these soils.

ABSORPTION OF POTASSIUM FROM A SOLUTION OF POTASSIUM CHLORIDE.

For studying the absorption of potassium by soils a solution of potassium chloride containing 200 parts per million of potassium was used. Three of the soils studied were the same as those used in the phosphate experiments, namely, the clay soil, the clay loam, and the fine sandy soil. In addition to these, two other soils were studied—a loam and a sand. The loam was a sample of the Leonardtown loam, from Leonardtown, Md., and the sand a sample of Sandhill, from Darlington, S. C.

The apparatus and general manipulations were the same as in the experiments already described. The soil was not previously washed with water, but was used in the air-dry form in which it had been kept for some weeks in the laboratory. The entire procedure is there-

fore comparable with that used for the sodium phosphate, where the dry soil was wet directly with the solution instead of previously by passing water through it. The apparatus was then filled with the solution as already described and regulated so as to have a flow of about 50 c. c. in twenty-four hours. The percolates were then analyzed for potassium by the colorimetric method described in a former bulletin.[a] In Table XXV are given the results obtained with the clay soil.

TABLE XXV.—*Absorption of potassium by a clay soil from a solution of potassium chloride containing 200 parts per million K.*

Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.		Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.		Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.	
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.
50	62	70	50	410	104	520	530	750	156	760	760
160	57	230	230	500	117	600	610	890	165	810	820
210	57	300	300	550	117	640	640	970	164	860	850
260	60	370	370	610	133	690	690	1,140	173	890	890
320	78	440	440	690	141	740	730				

In the first column appears the total number of cubic centimeters of solution passed through the soil, in the second column the concentration in potassium of the successive fractions, and in the third column the total quantity of potassium absorbed by the soil. The fourth column gives the calculated quantity of absorbed potassium obtained by a formula which will be described later. It will be noticed from the results in the second column that the first few hundred cubic centimeters of the 200 parts per million solution in passing through the soil was reduced to a concentration of approximately 60 parts per million and that in succeeding fractions this concentration gradually rises, showing a tendency to reach the original concentration of the solution, until when about 1,100 c. c. have passed it is 173 parts per million. At this point the soil has absorbed nearly 900 parts per million of potassium. The absorption obtained with the clay loam is given in Table XXVI.

TABLE XXVI.—*Absorption of potassium by a clay loam from a solution of potassium chloride containing 200 parts per million K.*

Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.		Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.		Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.	
		Observed.	Calculated.			Observed.	Calculated.			Observed.	Calculated.
C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	P. p. m.
50	101	50	60	500	167	340	340	1,060	178	510	510
100	99	100	100	680	164	400	410	1,240	175	550	540
350	125	290	270	880	167	470	470	1,390	180	570	560

[a] Bul. No. 31, Bureau of Soils, U. S. Dept. of Agr., 1906, p. 31.

The absorption of potassium by this soil is not so great as in the case of the clay soil, nor is it so great as the absorption of phosphate by this same soil; nevertheless the second column shows that the concentration of the first fractions of the 200 parts per million solution is reduced to approximately one-half in passing through the soil. As more solution passes the concentration rises and slowly approaches the original value, having risen to 180 parts per million when about 1,400 c. c. of the solution have passed through the soil, which at this point has absorbed nearly 600 parts per million of potassium. The results obtained with the loam are given in Table XXVII.

TABLE XXVII.—*Absorption of potassium by a loam from a solution of potassium chloride containing 200 parts per million K.*

Volume of perco-late.	Quantity K in so-lution.	Total quantity K ab-sorbed by soil.	Volume of perco-late.	Quantity K in so-lution.	Total quantity K ab-sorbed by soil.	Volume of perco-late.	Quantity K in so-lution.	Total quantity K ab-sorbed by soil.
C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.
80	100	80	210	82	240	390	120	410
110	72	120	280	90	320	460	128	460
150	69	170	320	106	350	690	150	580

With this soil the absorption is even more marked than with the clay loam, though less than with the clay. The first fraction is higher than the four succeeding ones. This is doubtless due to the same causes that produced the higher concentrations in the first fractions of the percolate obtained in the sodium phosphate experiments. This higher concentration of the first fraction is noticeable also with the two soils already described, although not so marked, and occurs likewise in the case of the succeeding soils, as will be seen presently. After reducing the solution to approximately 70 parts per million the concentration again rises until when about 700 c. c. had passed through the soil it was 150 parts per million. The experiment was not continued beyond this point. In Table XXVIII are found the results for the sandy loam.

TABLE XXVIII.—*Absorption of potassium by a sandy loam from a solution of potassium chloride containing 200 parts per million K.*

Volume of perco-late.	Quantity K in so-lution.	Total quantity K ab-sorbed by soil.	Volume of perco-late.	Quantity K in so-lution.	Total quantity K ab-sorbed by soil.	Volume of perco-late.	Quantity K in so-lution.	Total quantity K ab-sorbed by soil.
C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.	C. c.	P. p. m.	P. p. m.
50	104	50	220	141	180	740	172	290
100	96	100	300	171	200	910	180	330
150	126	140	520	185	230			

The absorption in the case of the sandy loam is much less than in the soils so far described, but it is nevertheless quite marked in the

first fractions of the solution passing through the soil. The absorption by the fine sand, given in Table XXIX, is still less, but definitely traceable in its effects on the various portions of percolate.

TABLE XXIX.—*Absorption of potassium by a fine sandy soil from a solution of potassium chloride containing 200 parts per million K.*

Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.	Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.	Volume of percolate.	Quantity K in solution.	Total quantity K absorbed by soil.
C. c.	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*
60	150	30	300	166	120	1,130	183	320
110	141	60	540	168	200	1,390	185	360
150	160	70	770	174	260			

REMOVAL OF ABSORBED POTASSIUM BY WATER.

The removal of the absorbed potassium from two soils was also studied, the soils used being the clay and the clay loam of the previous experiment. For this purpose the well-drained soils, containing 890 and 570 parts per million of absorbed potassium, respectively, were washed by filling the apparatus with distilled water and continuing the percolation at the same slow and constant rate used in passing the potassium solution. The percolate, collected in fractions, was analyzed for potassium as before. The results for the clay soil are given in Table XXX.

TABLE XXX.—*Removal of absorbed potassium from a clay soil by water.*

Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.	Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.	Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.	Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.	Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.
C. c.	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*
.....	.....	890	220	45	720	780	19	600	1,510	21	470			
40	171	820	310	29	700	840	19	590	1,640	19	440			
80	78	790	450	21	670	1,150	22	540	1,760	19	420			
130	56	770	520	19	650	1,260	20	520	1,870	17	400			
170	47	740	720	20	610	1,370	19	500	2,110	19	360			

The rather high concentration of the small fraction collected at the start is due to the stronger solution contained in the soil. On passing more water the percolate rapidly becomes weaker in potassium, until when about 450 c. c. have passed the concentration shows a practically constant composition of about 20 parts per million, although the percolation was continued until over 2,000 c. c. had been passed and the quantity of absorbed potassium in the soil reduced from nearly 900 to about 350 parts per million.

The removal of the absorbed potassium from the clay loam is shown in Table XXXI.

TABLE XXXI.—*Removal of absorbed potassium from a clay loam by water.*

Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.	Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.	Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.	Volume of percolate.	Quantity K in solution.	Total quantity K remaining in soil.
C. c.	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*	*C. c.*	*P. p. m.*	*P. p. m.*
....	....	570	200	43	440	660	30	310	830	26	260
70	89	510	330	31	400	720	28	290	880	25	250
140	59	470	470	30	360	780	30	270			

The results in this case are very similar to those of the clay soil, although the washing with water was not continued so long. The concentration of the solution is higher, showing the more ready removal of the potassium from this soil. When 800 c. c. of water had passed through the soil the concentration was 26 parts per million and the quantity of absorbed potassium had been reduced from 570 to about 250, whereas in the case of the clay the passage of a similar volume of water had reduced the soil from 890 to only about 600, and the concentration of the percolate had already dropped down to the constant concentration of approximately 20 parts per million.

GRAPHICAL REPRESENTATION AND DISCUSSION OF THE RESULTS OBTAINED WITH POTASSIUM CHLORIDE.

In figures 5 and 6 are given the curves for the results obtained in the experiments on the absorption of potassium, as well as those obtained in the removal of the absorbed potassium by water. In figure 5 are shown the results based upon the concentration of solution. The abscissas represent the volume of the solution or of water which has passed through the soil and the ordinates the concentration of potassium in the percolate. The upper boundary line of the figure gives the strength of the solution before passing through the soil, and the break in the curves gives the point where the solution was replaced by distilled water and the removal of the absorbed potassium was begun. Only the results for the clay and clay loam are given in this figure, as these are the two soils in which both the absorption and removal of potassium was studied. The absorption curve for the loam would lie between those of the clay and clay loam, the curves for the sandy loam and fine sand would lie above that of the clay loam. It is apparent from the figure that the general run of the absorption and removal of the potassium is very similar to the phosphate curves given in figure 2. The curves show that the concentration of the first few hundred cubic centimeters of the solution is materially reduced, in the one case approximately to one-half and in the other to one-fourth the original strength. With increase in volume of the solution passed the curves rise slowly and approach the upper boundary line of the figure (that is, the ordinate of the original strength of the solution) apparently as an asymptote.

The removal of the absorbed potassium is very rapid at first, but the solutions soon reach a constant concentration, as is very strikingly brought out by the horizontal position of the removal curve in both cases. A comparison with figure 6 also shows that the concentration of the solution becomes constant at a point where only about one-third of the absorbed potassium has been removed. It is also noteworthy that the clay, although it contains throughout a much larger quantity of absorbed potassium, gives a lower concentration of potassium in solution than does the clay loam with its smaller potassium content. It follows, therefore, that the relative concentration of the potassium

FIG. 5.—Solution curves. Absorption of potassium by soils from a solution of potassium chloride and the removal of the absorbed potassium by water.
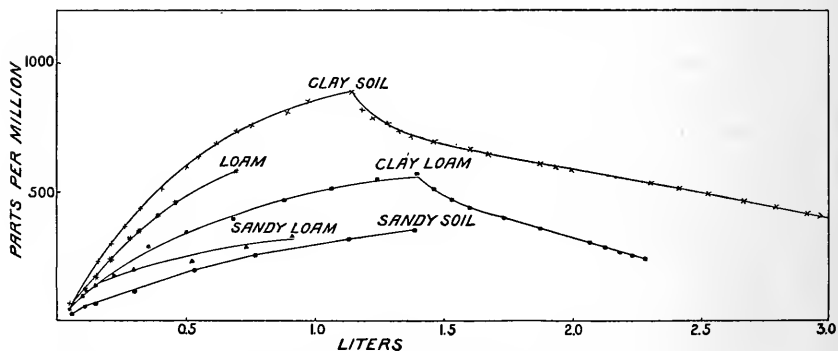

FIG. 6.—Soil curves. Absorption of potassium by soils from a solution of potassium chloride and the removal of the absorbed potassium by water.

in the percolates gives no indication of the quantity of absorbed potassium present in the soil, although it must be admitted that this is in a form readily soluble in water, as is shown by its continued removal by water in the above experiments. The magnitude of these absorption results and the removal of the absorbed material show very conclusively that in experiments dealing with the solubility of finely powdered substances of slight solubility, such as soils or rock-forming minerals, it is not so much the solubility itself with which one is dealing as with the decomposition and absorption phenomena and the removal of the absorbed products of decomposition.

In figure 6 are shown the results expressed in terms of the soil itself, the abscissas being the volume of solution or water passed through the soil, and the ordinates the amount of potassium absorbed by the

soil.   It is at once apparent that the different soils show marked dif-
ferences in their absorptive power for potassium.   The clay loam, for
instance, is approaching a saturated condition with a concentration of
potassium in the soil at which the clay soil is still absorbing at a rapid
rate.   Similar differences in the extent of the absorption are shown by
the other soils, but the general run of the curves is the same as those
of the more thoroughly studied clay soil and clay loam.   The removal
curves drop rapidly at first and then run downward in a straight line
in the case of both of the soils studied.

The similarity of the absorption curves to those of the phosphate
given in figure 3, in that they tend to approach a horizontal asymptote,
is striking.   It has been found that these results are quite accurately
described by the same differential equation which describes the phos-
phate-absorption curves.

$$\frac{dy}{dv} = K(A - y)$$

or integrating

$$\log (A - y) = \log A - Kv$$

where K is a constant and A is the maximum amount of potassium
the soil can absorb under the conditions of the experiment—i. e., A is
the specific absorptive capacity of the soil for potassium, y is the
amount of potassium the soil has absorbed when the volume v of solu-
tion has passed through the soil.   In these experiments, however, as
in the case of the sodium phosphate, on account of the fact that the
curves do not pass through the origin, it is necessary to substitute log
$(A - y_0)$ for $\log A$, where y_0 is the ordinate of the point taken as the
first reading, and also to substitute the value of $(v - v_0)$ for v where v_0
is the volume corresponding to the y_0 taken as the first reading.   The
formula has been applied to the results obtained with the clay and the
clay loam.   When the following values are used a very good agree-
ment between the experimental results and the calculated results is
found to exist.

	A.	$\log (A - y_0)$.	K.
Clay soil	1,000	2.886	0.000864
Clay loam	650	2.740	.000622

The method of calculation is exactly the same as already described
with the phosphate absorptions.   The calculated results for the respec-
tive soils are given in the fourth columns of the absorption tables.
In figure 6 the absorption curves for the clay and the clay loam are
drawn through the calculated points, the experimental points being
indicated by the respective signs and the plots show, therefore, how
well the calculated and found figures agree.

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SUMMARY.

The data presented in the foregoing pages throw much new light on the behavior of phosphates and potassium in the soil. The successive solutions obtained by slow percolation of water through the four soils have been shown to have a concentration in phosphate which is practically a constant for any given soil, thus substantiating the experiments of Schloessing and other authorities, as well as the conclusions advanced in former publications from this Bureau deduced from entirely different lines of evidence. The soils studied, moreover, yielded solutions which differed little in concentration, except in the case of the Podunk fine sandy loam, which has a low absorptive capacity and is acted upon by water to an unusual extent.

The absorption experiments with the phosphates have shown that at the start this is very rapid and complete, the strong phosphate solution being reduced to the concentration characteristic of the water solution for that soil. This seems to show that the application of considerable quantities of a soluble phosphatic fertilizer would not materially increase the concentration of the phosphate dissolved in the free soil moisture. On tracing the absorption of phosphate further, by the percolation of more phosphate solution, it has been found that while absorption continues it is becoming less marked and finally a saturated condition will be reached. The law which appears to govern this change has been found to be that the quantity absorbed from a unit volume of the phosphate solution as it passes through the soil is proportional to the quantity which may yet be absorbed. This absorption process is mathematically represented by the differential equation

$$\frac{dy}{dv} = K(A - y)$$

where K is a constant, A the maximum quantity the soil can absorb, and y the quantity it has absorbed when the volume v of phosphate solution has passed through the soil. The quantity A is defined as the specific absorptive capacity of the soil. The value of A differs considerably for the different soils, being highest in the clay and lowest in the sandy soil. In the case of the clay and the clay loam the same values were found with the sodium phosphate as with the monocalcium phosphate, but in the fine sandy loam and fine sand these two phosphates gave entirely different results, the specific absorptive capacity with the monocalcium phosphate being over twice as great as with the sodium phosphate.

The removal of the absorbed phosphate appears to be in general the same as the removal of the phosphate from the original soil. The concentration of the percolates becomes constant when only a fractional part of the absorbed phosphate has been removed, and this concentration is practically that yielded by the original soil with a far less phosphate content. It would therefore seem that the concentration of the phosphate in the soil solution is practically the same, whether the soil contains a large or a small quantity of absorbed phosphate, and that it is this absorptive power of the soil which controls the concentration of the phosphate in the free soil moisture. It follows that with change in the absorptive power of the soil the concentration of the phosphate in the free soil moisture would also change. Attention has been called to the unusual extent to which the Podunk fine sandy loam is acted upon by water. It is therefore interesting to note that the concentrations of the phosphate in the aqueous percolates from this and the other three soils came closer together after the soils had been treated for some time with the calcium or sodium phosphate solution than they did before this treatment. This seems to indicate that by the similar treatment of the soils with considerable quantities of the same chemical substances the soils have been made more alike in their chemical behavior toward water, so far as phosphate—the only constituent studied in this case—is concerned. It is also noteworthy that the absorbed phosphate is not insoluble, but is slowly and continuously diffusing into the free soil moisture and becoming, therefore, directly available to plants.
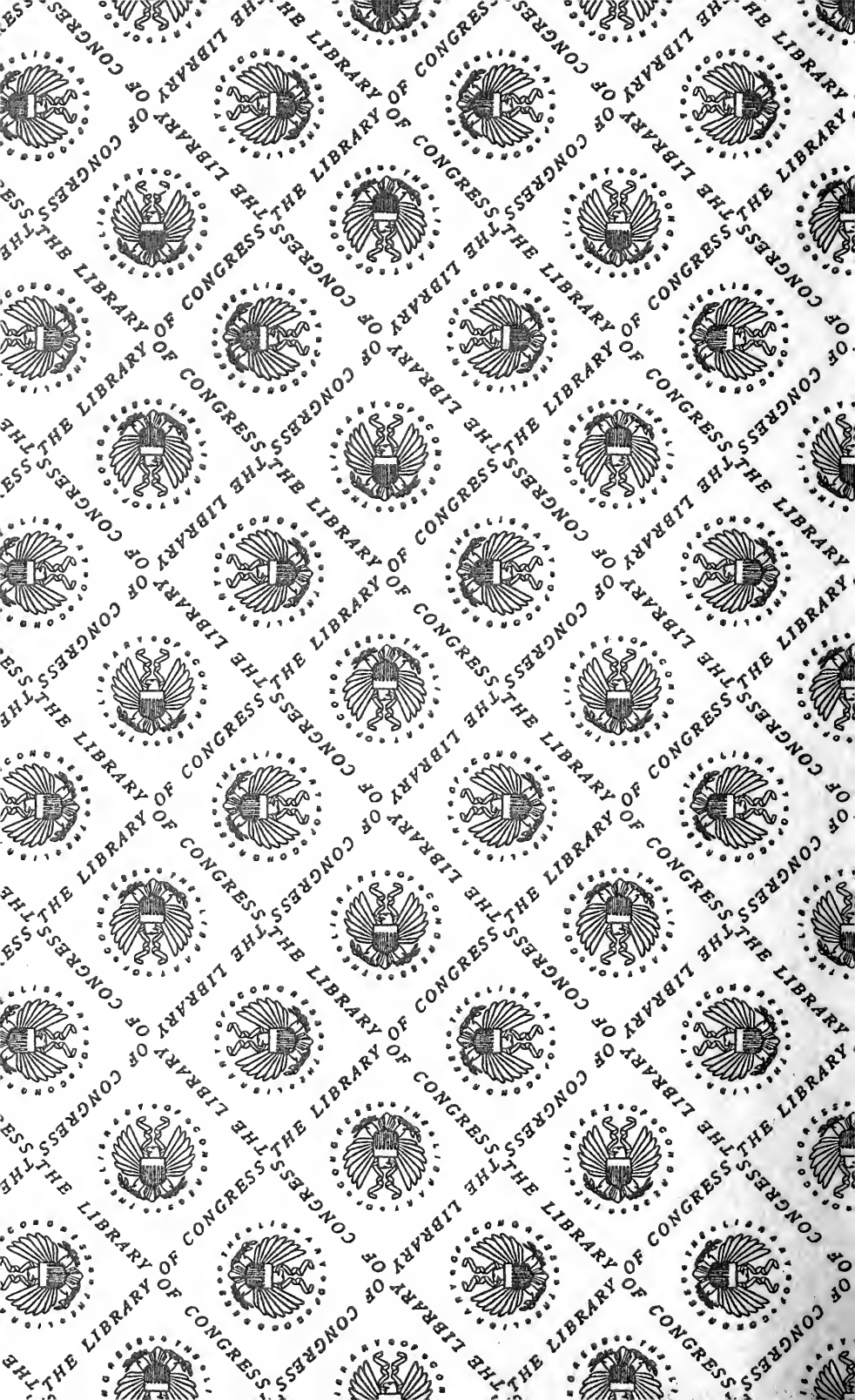
The results obtained in the potassium experiments, while not so comprehensive, nevertheless show the same general tendencies. The five soils studied for their absorption all show a more or less marked absorptive power for potassium, which is, however, considerably less than the absorptive power of these soils for phosphate. The law governing the absorption process appears to be the same with potassium as with phosphate, and the curve of the absorption is quite accurately described by the same differential equation:
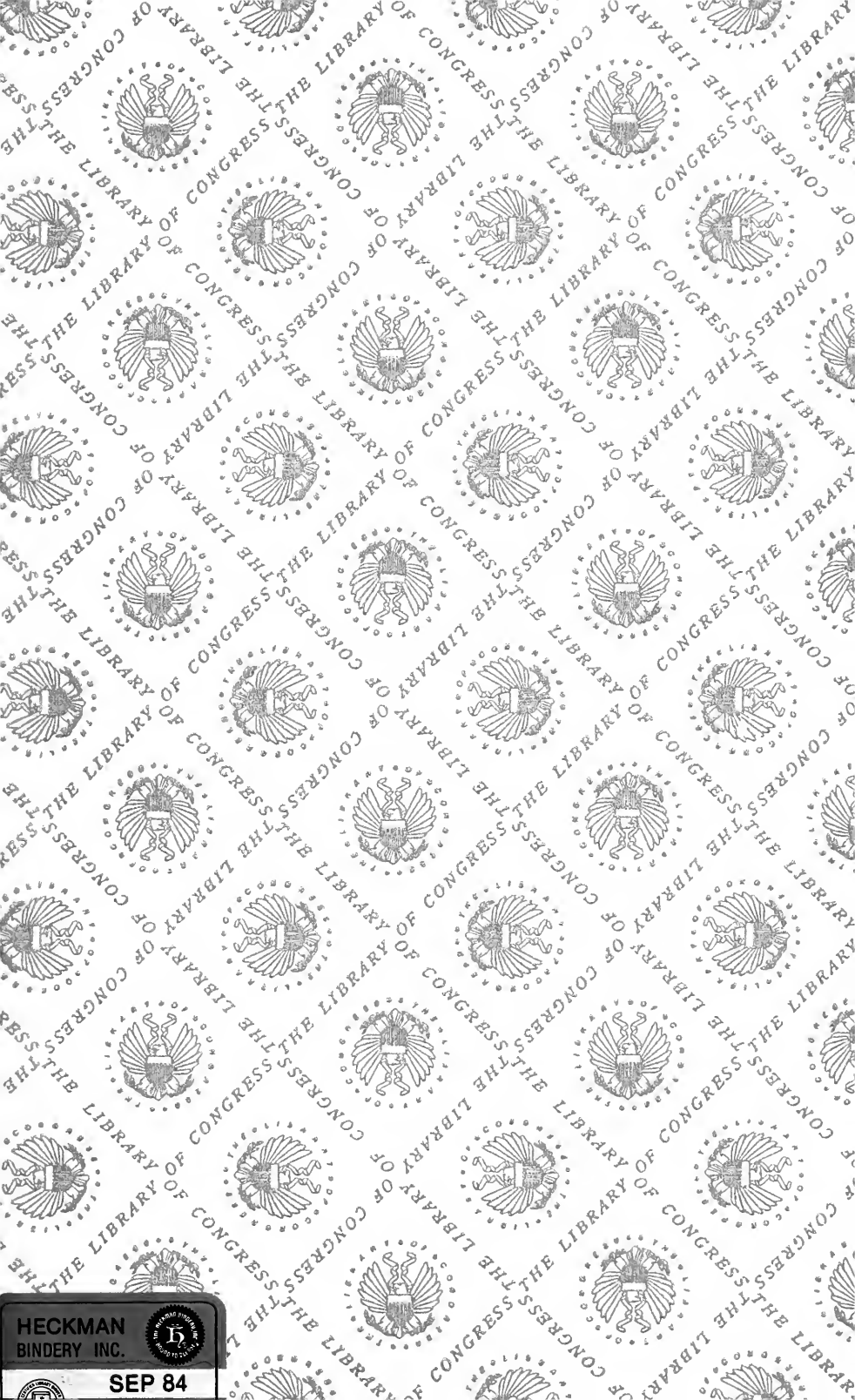
$$\frac{dy}{dv} = K(A - y)$$

The constancy of the removal of the absorbed potassium by water is even more striking than in the case of the phosphate and the conclusion that the concentration in the free soil moisture is dependent on the absorptive power of the soil is well sustained by these results. The absorbed potassium, like the absorbed phosphate, is continually diffusing into the free soil moisture and becoming, therefore, directly accessible to plants.

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