INVESTIGATIONS ON THE RÔLE OF SILICON
IN PLANT NUTRITION.

Part II. Adsorption of Silica in Soluble Forms by Colloidal Oxides of Iron and Aluminium.

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IN a previous communication (Sreenivasan, 1935) it has been shown that when a soluble silicate is added to the soil, part of it, depending upon the concentration in solution, the nature of the soil and, to some extent, its moisture content, is rendered insoluble almost immediately after addition and that the seat of interaction between the soil and silicate is in the colloidal fraction and is probably almost entirely due to the mineral colloids of the soil. Since when Van Bemmelen (1879, 1888, 1900, 1904) pointed out the colloidal properties of the soil, several investigators have studied adsorption phenomena in clays where these latter have been treated as a whole, but in most of the work thus far done, the systems have been so complex that it has not been possible to say whether one had physical adsorption or chemical combination or both. It was considered therefore that a better insight into the nature of interaction between the soil and soluble silicates could be obtained by working with pure colloids. The natural inorganic colloids of the soil are composed mainly of colloidal silica, iron oxide and alumina. In fact they represent adsorption compounds of indefinite composition formed by the mutual precipitation of colloidal hydroxides of opposite charges. A few workers have studfed the adsorption of various salts by pure colloids like iron oxide and alumina. Thus Gordon and his co-workers (1922, 1923), Miller (1928), Ghosh and Bhattacharya (1930) and others have thrown useful light on the rôle of soil colloids in plant nutrition and as to how some salts in certain forms become available for plant food.

In the present investigation, adsorption of silica from solutions of sodium silicate and from silica sol by pure hydrogels of iron oxide and alumina has been studied. The adsorption by these colloids of silica under different hydrogen-ion concentrations has also been followed as it was hoped that

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such work might explain how acidity or alkalinity of soil affects silicate adsorption and its usefulness, direct or indirect, as plant food.

Experimental.

Hydrogels of iron oxide and alumina were prepared by addition of ammonium chloride and ammonia to solutions of ferric chloride and aluminium sulphate respectively. The precipitates were allowed to settle and washed by repeated decantation with distilled water until the supernatants were free from ammonia and chloride or sulphate as the case may be. As much of the water as possible was now syphoned off and the suspensions stocked as such.

Sodium silicate solution was made by diluting Kahlbaum's 25 per cent. sodium silicate to ten times its volume and stocking it as such after filtration. The silica in a known volume of this solution was determined in the manner previously described (Sreenivasan, *loc. cit.*).

Silica sol was obtained in pure condition by continued dialysis, for over 10 days, of a mixture obtained by slowly adding sodium silicate solution to

TABLE I.

Silicate added (as mg. of silica in 200 c.c. of solution)	Initial P_H of silicate solution	Silicate in solution after adsorption (as mg. of silica)	Silica retained by gel (mg.)	Per cent. retention of silica	Retention of silica per g. of dry gel (mg.)	P_H of silicate solution after adsorption
Ferric hydroxide gel = 376·0 mg. Fe_2O_3.　P_H = 7·6.						
75·1	8·6	10·0	65·1	86·7	173·2	8·4
125·1	9·0	42·0	83·1	66·4	221·0	8·6
250·2	9·2	130·1	120·1	48·1	319·4	8·8
375·3	9·5	224·2	151·1	40·3	401·9	9·2
500·4	9·7	327·9	172·5	34·5	458·6	9·6
Alumina gel = 157·0 mg. Al_2O_3.　P_H = 8·0.						
75·1	8·6	23·9	51·2	68·1	326·1	8·6
125·1	9·0	55·8	69·3	55·3	441·2	8·8
250·2	9·2	160·0	90·2	36·1	574·5	9·2
375·3	9·5	280·1	95·2	25·4	606·3	9·6
500·4	9·7	367·9	132·5	26·5	843·9	9·8

dilute hydrochloric acid until the latter was just in excess of the former. Dialysis was done in a parchment membrane and until free from chloride.

Effect of addition of different quantities of sodium silicate to iron and alumina gels.—10 c.c. of each of the gels (containing respectively 376 and 157 mg. of iron oxide and alumina) were taken in stoppered bottles and treated with 200 c.c. of a solution containing different known quantities of silicate. The mixture was in each case shaken repeatedly and let stand overnight so that equilibrium might be attained. They were then filtered and the silica in aliquots estimated. The H-ion concentration of the silicate solution before and after adsorption was also determined colorimetrically using a Hellige comparator outfit. The total silica in solution was calculated, the water present in the gels being also taken into account so that the retention of silica by the gels was expressed on their dry weight. The results are given in Table I.

In another set of experiments, identical quantities of the silicate as in the above, but in 100 c.c. of solution were added to the same weights of the gels so that although the amount of silicate was the same as before, its concentration was in each case double that previously used. The results are given in Table II.

TABLE II.

Silicate added (as mg. of silica in 100 c.c. of solution)	Iron hydroxide = 376·0 mg. Fe_2O_3				Alumina = 157·0 mg. Al_2O_3.			
	Silicate in solution after adsorption (as mg. of SiO_2)	Silica retained by gel (mg.)	Retention of silica per cent.	Silica retained per g. of dry gel (mg.)	Silicate in solution after adsorption (as mg. of SiO_2)	Silica retained by gel (mg.)	Retention of silica per cent.	Silica retained per g. of dry gel (mg.)
125·1	39·2	85·9	68·7	228·4	43·6	81·5	65·2	519·2
200·2	70·0	130·2	65·0	346·1	76·7	123·5	61·7	786·5
250·2	114·1	136·1	54·4	361·9	132·2	118·0	47·2	751·6
375·3	220·1	155·3	41·4	413·0	271·7	103·6	27·5	659·8
500·4	306·4	194·0	38·9	515·9	342·4	158·0	31·6	1007·0

It would be seen from Tables I and II that adsorption similar to that observed in the case of soil (Sreenivasan, *loc. cit.*) takes place also in the case of the gels of iron oxide and alumina. While as with the soil, the percentage adsorption decreases with increasing amounts of added silicate, a comparison

between Tables I and II will show that adsorption is greater for the same amount of added silicate when it is present in half the volume of the solution. A comparison of the figures for the retention of silica per gram of dry gel would show that alumina retains nearly twice as much of silica as iron hydroxide gel.
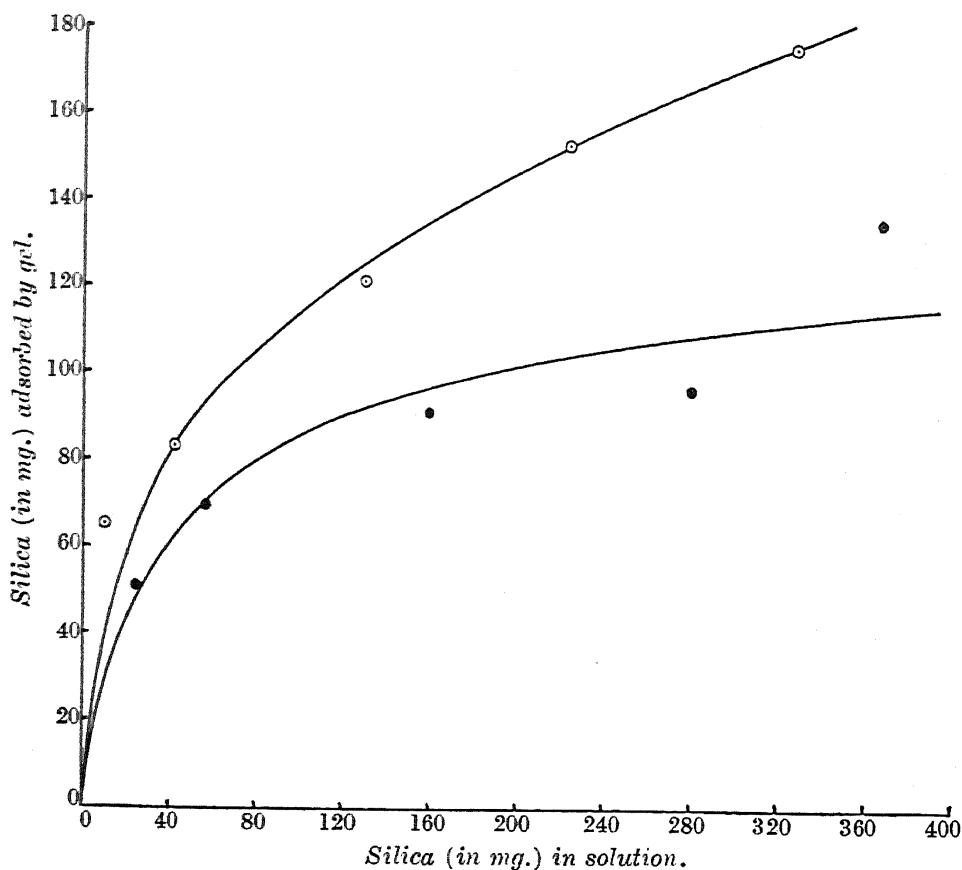

Fig. 1. Adsorption of silicate by gels of iron oxide and alumina.
o—o Ferric hydroxide gel.
•—• Aluminium hydroxide gel.

In Fig. 1, the amount of silica retained by the gels of alumina and iron hydroxide (Table I) have been plotted against the corresponding quantities present in solution. It is seen that the process is an ordinary adsorption obeying more or less the usual logarithmic proportionality law expressed by Freundlich (cf. Sreenivasan, loc. cit.).

In the above experiments the quantities of silicate added were probably far in excess of the actual weights of the adsorbing compounds—viz., iron oxide and alumina and hence the results may not be strictly comparable to the previous studies on soil and silicate solutions. Hence in the following experiments the proportion of hydrogels to silicate was increased. The amount of silica in solution was estimated as before (Table III).

TABLE III.

Silicate added (as mg. of silica in 150 c.c. of solution)	Iron hydroxide = 1432 mg. Fe_2O_3				Alumina = 1056 mg. Al_2O_3			
	Silicate in solution (as mg. of SiO_2)	Silica retained (mg.)	Percentage of silica retained	Silica retained per g. of dry gel (mg.)	Silicate in solution (as mg. of silica)	Silica retained (mg.)	Percentage of silica retained	Silica retained per g. of dry gel (mg.)
122·3	14·2	108·1	88·4	75·5	12·6	109·7	89·7	103·9
244·6	42·4	202·2	82·7	158·4	36·1	208·5	85·3	197·6
366·9	69·8	297·1	81·0	207·5	71·9	295·0	80·4	279·4
489·2	96·7	392·5	80·2	274·1	88·6	400·6	81·9	379·3

As in previous experiments quite a large part of the added silicate is retained by the colloidal hydroxides. It would be seen, however, that with increasing concentration of silicate the fall in percentage retention is not so rapid as in previous experiments.

Adsorption of silica from silica sol by hydrous iron oxide and alumina.— In the following experiments known quantities of silica sol were used instead

TABLE IV.

Silica sol added (as mg. of silica)	Initial P_H of silica sol	Silica in solution after adsorption (mg.)	Silica retained by gel (mg.)	Per cent. retention of silica	Silica adsorbed per g. of dry gel (mg.)	P_H of silica sol after adsorption
Iron hydroxide gel = 286·4 mg. Fe_2O_3						
44·6	4·8	13·9	30·7	68·8	107·2	7·0
89·1	5·8	81·5	57·6	64·7	201·1	6·8
133·7	6·2	52·0	81·7	61·1	285·2	6·4
178·2	6·2	99·9	78·3	44·1	273·4	6·4
Alumina gel = 211·2 mg. Al_2O_3						
44·6	4·8	8·0	36·6	82·1	173·3	7·4
89·1	5·8	28·0	61·1	68·6	289·3	7·0
133·7	6·2	47·2	86·5	64·7	409·6	7·0
178·2	6·2	66·6	111·6	62·6	528·3	6·8

of sodium silicate. The procedure was the same as before. The results are given in Table IV.

The P_H of the silica sol itself was 4·0 while that of the 1 : 10 diluted sol was 5·8.
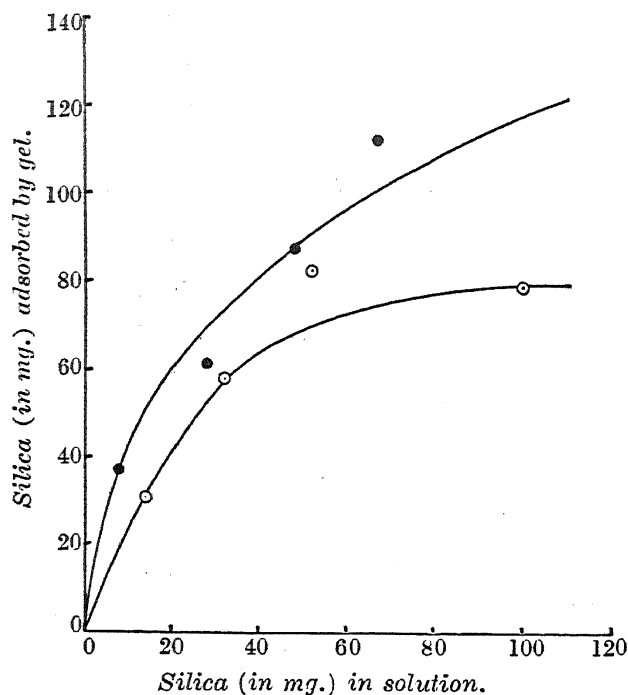

FIG. 2.   Adsorption of silica sol by hydrogels of iron
oxide and alumina.

⊙—⊙ Ferric hydroxide gel.
●—● Alumina gel.

The quantities of silica adsorbed by the gels have been plotted against the corresponding amounts in solution (Fig. 2). The results thus show that even when silica sol is used instead of sodium silicate, adsorption occurs to a considerable extent. In this respect silicate adsorption is different from phosphate adsorption because the latter is adsorption of an anion, whereas the present phenomenon would appear to be that of a negative colloidal complex by a positive colloid.

Influence of hydrogen-ion concentration on the extent of retention of silica by gels of iron oxide and alumina.—Since it is known that hydrions and hydroxylions are the most strongly adsorbed ions, it would follow that the adsorption of silica by the colloidal oxides of aluminium and iron would be modified in the presence of one or other of these ions.   It would be of interest therefore to determine the extent of adsorption of silica under varying hydrogen-ion concentrations.

Known amounts of the hydrogels of iron oxide and alumina were treated with 200 c.c. of a silicate solution containing a definite quantity of silica but adjusted to different hydrogen-ion concentrations by means of decinormal hydrochloric acid or sodium hydroxide as the case may be. The mixture was well shaken and after allowing to let stand overnight, filtered and the silica in filtrate determined. Tables V and VI give the results obtained using different amounts of the two gels and different concentrations of the silicates.

TABLE V.

Initial P_H of silicate solution (200 c.c.)	Iron hydroxide gel = 376·0 mg. Fe_2O_3					Alumina gel = 157·0 mg. Al_2O_3				
	P_H of solution after adsorption	Silica in solution (mg.)	Silica retained (mg.)	Per cent. retention of silica	Silica retained per g. dry gel. (mg.)	P_H of silicate after adsorption	SiO_2 in solution (mg.)	Silica retained (mg.)	Per cent. retention of silica	SiO_2 retained per g. dry gel (mg.)
2·5	2·8	304·8	195·6	39·1	520·1	2·8	347·2	153·2	30·6	975·9
5·0	5·8	311·6	188·8	37·7	502·3	6·0	362·0	138·4	27·7	881·6
7·0	8·4	318·8	181·6	36·3	482·9	8·4	369·2	131·2	26·2	835·6
9·0	9·6	327·2	173·2	34·6	460·6	9·8	366·4	134·0	26·8	853·5
10·6	10·0	337·0	163·4	32·7	434·6	10·2	354·0	146·4	29·3	932·8

Silicate added (as mg. of silica) = 500·4.

TABLE VI.

Initial P_H of silicate solution (100 c.c.)	Iron hydroxide gel = 572·8 mg. Fe_2O_3					Alumina gel = 422·4 mg. Al_2O_3				
	P_H of solution after adsorption	SiO_2 in solution (mg.)	SiO_2 retained (mg.)	Per cent. retention of silica	SiO_2 adsorbed per g. dry gel (mg.)	P_H of solution after adsorption	SiO_2 in solution (mg.)	SiO_2 retained (mg.)	Per cent. retention of silica	SiO_2 adsorbed per g. dry gel (mg.)
4·0	5·2	18·0	104·3	85·3	182·1	5·2	14·0	108·3	88·5	256·4
5·0	6·4	20·4	101·9	83·4	177·8	6·6	19·6	102·7	84·0	243·2
7·0	7·4	22·6	99·7	81·5	174·1	7·8	24·2	98·1	80·2	232·3
9·0	7·8	29·2	93·1	76·2	162·5	8·4	26·4	95·9	78·3	227·1
10·6	8·6	41·0	81·3	66·5	141·9	8·8	24·0	98·3	80·4	232·8

Silicate added (as mg. of SiO_2) = 122·3.

It would be seen from the above that as the P_H of the silicate solution changes from the acid side towards alkalinity, there is a gradual decrease

in the percentage retention of silica by iron gel, while with alumina there is also a decrease as the P_H increases though when the reaction is very alkaline, as at P_H 10·2, retention of silica appears to increase again. It is probable that, although the extent of hydrolysis of sodium silicate will be far less in both acid and alkaline regions the increased retention of silicate observed at low P_H may be due to a part of the iron or alumina gel being brought into solution only to be precipitated again as the corresponding silicate. Since alumina gel is amphoteric and is therefore soluble at very high P_H as well, this will explain the high retention of silica by alumina in alkaline medium. With iron hydroxide, however, at high P_H no iron is soluble and, besides, there will be a suppression of hydrolysis of the sodium silicate. The adsorption of silica is therefore less in this case. It may be noted that other workers (Mattson, 1927, 1931 ; Gordon and co-workers, *loc. cit.*) have made similar observations with regard to the adsorption of phosphate ion by soil colloids and found that adsorption decreases with increased P_H values and *vice versa*.

Influence of Hydrogen-ion concentration on the adsorption of silica from silica sol by gels of iron oxide and alumina.—The use of solutions of sodium silicate of different hydrogen-ion concentrations naturally brings about variations in the extent of hydrolysis of the silicate solution. Hence any change in the retention of silica from sodium silicate solutions of varying P_H may be due to the varying degrees of hydrolysis of the sodium silicate or to the change in reaction itself. In the following experiments pure silica sol adjusted to different H-ion concentrations by addition of decinormal acid or alkali was used so that the effects due to hydrolysis were eliminated.

TABLE VII.

Initial P_H of silica sol	Iron oxide gel = 286·4 mg. Fe_2O_3					Alumina gel = 211·2 mg. Al_2O_3				
	P_H of solution after adsorption	SiO_2 in solution (mg.)	SiO_2 retained (mg.)	Per cent. retention of silica	SiO_2 retained per g. dry gel (mg.)	P_H of solution after adsorption	SiO_2 in solution (mg.)	SiO_2 retained (mg.)	Per cent. retention of silica	SiO_2 retained per g. dry gel (mg.)
2·0	3·0	57·4	120·8	67·8	345·9	2·6	37·5	140·7	79·0	297·5
4·0	4·8	80·2	98·0	55·0	280·6	4·0	49·6	128·6	72·2	271·6
5·0	6·0	109·0	69·2	38·8	198·2	6·0	71·1	107·1	60·1	226·2
10·6	9·6	115·0	63·2	35·5	181·0	9·0	65·3	112·9	63·4	238·4

Silica sol added (as mg. of silica) = 178·2.

Known amounts of the hydrogels of iron oxide and alumina were treated in well-stoppered bottles with the same volume (100 c.c.) of a solution of silica sol adjusted as before to different initial P_H values. The mixture was well shaken, let stand overnight and then filtered. The P_H of filtrate was determined and the silica in aliquots estimated. The amount of silica in solution was then calculated, all the water of hydration of the gel being considered as water of dilution in order that minimum adsorption might be shown. The results are given in Table VII.

Similar change in the amounts of silica retained with increasing P_H is observed as in the experiments with sodium silicate. Thus, in the case of iron hydroxide gel there is a regular decrease in adsorption as the P_H increases, but with alumina there is a decrease followed by a slight increase at high P_H. The decrease in adsorption with increased P_H may be due to the presence of hydroxyl ions which might be preferentially adsorbed by the gels. Alumina gel, not being so electro-positive in alkaline medium as iron gel, would have less affinity for hydroxyl ions and consequently more of silica is retained.

Successive washings of the gel-silica complex.—Known amounts of the gels of iron oxide and alumina were treated in stoppered bottles with definite volumes of sodium silicate, shaken well and allowed to remain overnight. The mixture was then filtered and the residue on the filter paper washed with successive 100 c.c. portions of hot water and the silica in filtrates determined separately. The results are given in Table VIII.

TABLE VIII.

	Iron gel (286·4 mg. Fe_2O_3)	Alumina gel (211·2 mg. Al_2O_3)
Silica added as silicate ..	249·0 mg.	
Silica recovered from solution (mg.)	142·6	134·4
	Silica in 100 c.c. of wash water from gel-silica complex (mg.)	
First 100 c.c.	34	46
Second 100 c.c.	12	10
Third 100 c.c.	4	6
Fourth 100 c.c.	Nil	Nil

The first washings give an appreciable quantity of the silica, probably due to the latter having been mechanically held by the gel and being washed away rather than due to any solvent action on the complex. Subsequent washings give practically no silica in solution, thereby suggesting that a fairly stable adsorption complex is formed.

Discussion.

It has been shown in the previous investigation (Sreenivasan, 1935) that the interaction between soil and sodium silicate solutions is mainly accounted for through adsorption by the mineral soil colloids. The present enquiry with single colloidal materials like hydrous alumina and iron oxide has confirmed that it is through the phenomenon of adsorption that silica is retained by the colloids. This would also show the similarity between the colloidal properties of the soil and those of gels of alumina, iron oxide and silica, first pointed out by Van Bemmelen (*loc. cit.*) and later on emphasised by a number of other workers (Whitney, 1921; Gordon, 1922; Anderson and Mattson, 1925; and others). The colloidal soil material is chiefly made up of silica, alumina, iron oxide, organic matter (humus) and combined water. These divide themselves electro-kinetically into positive and negative colloids. Silica and humus are strictly electro-negative (though silica gel is electro-positive at very low P_H, *i.e.*, in the region of P_H 1·2). They adsorb and combine with bases. The sesquioxides are electrical ampholytes, being electro-positive in acid and electro-negative in alkaline solutions (Mattson, 1930). Thus, the study of the influence of hydrogen-ion concentration has shown that adsorption decreases with increase in P_H. This is to be expected because, due to the presence of excess of hydroxylions as the acidity decreases, the absorptive properties of the hydrogels will be weakened by saturation with hydroxyl ions. In the case of alumina gel, however, silicate retention is greatest both at low and at high P_H. This is of course due to the especially pronounced amphoteric character of that colloid.

Since at low P_H it can be assumed that the hydrolysis of sodium silicate will be negligible and since even then silicate adsorption occurs to a considerable extent, it would follow that silicate adsorption proceeds independently of the extent of hydrolysis of sodium silicate. This would support the earlier view (Sreenivasan, *loc. cit.*) in regard to the composition of sodium silicate, *viz.*, that it is essentially a mixture of alkali and silicic acid sol. It is possible that conductivity determinations of solutions of sodium silicate mixed with varying known amounts of acid and alkali would throw more light on the nature and behaviour of this compound in solution.

The possible beneficial effects of silicate adsorption in releasing from combination certain fertilising ingredients which may not otherwise become available to plant nutrition has been indicated elsewhere (Sreenivasan, 1934). Although the adsorbed silicate is firmly retained by the colloidal hydroxides, being only removed in traces by leaching with water, yet nothing is known as to how far the adsorption complex is stable in the presence of other ions such as the phosphate. Further work along these lines would help to throw light on the mode of action of silica in inducing greater phosphorus intake by plants.

Summary.

(1) When a solution of sodium silicate is added to hydrogels of iron oxide or alumina there is considerable adsorption of silicate similar to that observed in the case of the soil. Retention of silica is greater in the case of alumina than with iron oxide gel and the percentage retention decreases with increasing concentration.

(2) Similar adsorption of silica occurs in the case of ferric, or aluminium hydroxide gel—silica sol systems.

(3) Study of the influence of hydrogen-ion concentration on extent of silica retention shows that as the P_H of the medium increases, there is a decrease in the retention of silica by the gel. With alumina gel at high P_H, however, there is greater adsorption. This is due to the amphoteric nature of alumina.

(4) The adsorbed silicate is firmly retained by the colloidal gel and is not leached out by water.

(5) The possible significance of silicate adsorption in relation to phosphorus resorption in soils is indicated.

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