THE POTENTIAL ACIDITY OF SOILS

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Since Bjerrum (5) in his first two papers in a series on the causes of actual and potential² acidity of soils pointed out the great theoretical value of the knowledge of these properties, very few have worked on this subject.

The author, when investigating these soil characters, especially on some Oriental soils (1, 3, 4) found results which may be of both theoretical and practical value.

Chiefly, there are two different methods for measuring hydrogen-ion concentration, viz., electrometric and colorimetric. All measurements in this work are made according to the colorimetric method as modified by Gillespie (8). The accuracy of this method to the first decimal is quite sufficient for soil investigations where the deviations are so great, and it is so convenient that it can be used under conditions where no laboratory equipment is available.

The hydrogen-ion concentration was measured in soil extract made up as follows:

Ten grams natural moist soil were shaken with 50 gm. distilled water and then left to settle. The next day the extract was filtered and the pH value of the filtrate was determined. By this method there was introduced a source of error, viz., the probable change in the pH value of the soil solution when diluted. Sharp and Hoagland (14), however, give experimental data for the correctness of this method when not too large amounts of water are used.

The potential acidity in the following experiments was measured as follows:

In a series of flasks, usually nine, 5.00 gm. soil was introduced into each and then 10, 5, 2 and 1 cc. of about 0.1 *N* acid, or the same amounts of alkali was added, except in the case of the check, and the solution made up to 20 cc. with distilled water. The flasks were then corked, shaken for a time and left to settle. The whole procedure takes one day. After filtering, the pH values were determined colorimetrically in the filtrate. The amount of acid or alkali added is calculated in cc. of 0.1 *N* solution per gram of dried soil 100° C.

Sometimes stored soils have been used for hydrogen-ion concentration investigations and in order to determine the influence of drying on both the actual and potential acidity, the following experiment was carried out.

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² Here actual acidity means the same as hydrogen-ion concentration. Potential acidity means the changes in actual acidity obtained when acids or alkalies are added.

A humus-rich soil was put into four different beakers. One was covered with a glass and kept in the dark and at constant temperature; one was dried at room temperature (varying between 15° and 20°C.); one was dried at 100°C. and one at 150°C. After 14 days, the titration curves were made. Results are shown in table 1. From this it is seen that within the experimental error the results are quite congruent and the different treatment did not influence the acidity of the soil.

TABLE 1
The influence of drying on soil acidity

KIND OF SOIL		TREATED WITH 0.1 N H ₂ SO ₄					TREATED WITH 0.1 N NaOH				
A. Natural moist soil.....	cc.	2.50*	1.25	0.50	0.25	0.00	0.13	0.26	0.65	1.2	
	pH	4.3	5.2	6.2	7.0	7.2	7.3	7.3	7.4	8.0	
B. Air dried 15-20°C.....	cc.	2.62	1.51	0.52	0.26	0.00	0.13	0.27	0.67	1.33	
	pH	4.0	4.8	6.3	7.0	7.2	7.2	7.3	7.4	8.0	
C. Steam dried 100°.....	cc.	2.60	1.30	0.52	0.26	0.00	0.13	0.27	0.66	1.33	
	pH	4.1	5.3	6.3	7.0	7.2	7.3	7.3	7.4	8.0	
D. Heat dried 150°.....	cc.	2.50	1.25	0.50	0.25	0.00	0.13	0.26	0.64	1.27	
	pH	4.3	5.3	6.3	7.0	7.2	7.3	7.3	7.4	8.0	

* In this, as well as tables 2 and 5-9, figures in italics show the amount of acid or alkali which has been added to the soil while the regular type shows the resulting reaction.

TABLE 2
The influence of different acids and alkalis on soil reaction

ACID ADDED		TREATED WITH 0.1 N ACID					ALKALI ADDED		TREATED WITH 0.1 N ALKALI				
A. H ₂ SO ₄	cc.	2.42	1.21	0.48	0.24		NaOH	cc.	0.00	0.12	0.25	0.61	1.22
	pH	3.1	4.1	5.0	6.2			pH	7.0	7.4	7.8	8.4	9.3
B. HCl.	cc.	0.43	0.22	0.11	0.05		KOH	cc.	0.00	0.04	0.08	0.17	0.34
	pH	5.7	6.3	6.6	6.8			pH	7.0	7.4	7.6	8.0	8.5
C. HNO ₃	cc.	0.32	0.16	0.08	0.05		H ₄ NOH	cc.	0.00	0.05	0.08	0.16	0.32
	pH	0.9	6.3	6.7	6.9			pH	7.0	7.2	7.5	7.8	8.1
D. CH ₃ COOH...	cc.	0.35	0.18	0.09	0.05		Ba(OH) ₂	cc.	0.00	0.05	0.06	0.20	0.41
	pH	5.0	5.5	5.9	6.9			pH	7.0	7.4	7.6	8.0	8.5
After 3 days.....	pH	(5.6)		(6.0)				pH					

A short storage, therefore, as for transportation etc., does not interfere with the work, but one must be very careful with soils stored for a long time.*

Another objection is that one may obtain different results when using different acids or alkalis. In order to control this the titrations were made in

* In the case of the Java or Egyptian soils, where stored soils also were employed in the work, tests with the fresh field soil gave the same results as the stored ones.

four series, using H_2SO_4 , HCl , HNO_3 and CH_3COOH , as acids, and NaOH , KOH , NH_4OH and $\text{Ba}(\text{OH})_2$ for the alkalies. The results of these tests are given in table 2, which shows that within the limits of experimental error, equivalent amounts of acid or alkali caused equal changes except in the case of acetic acid which gave a higher acidity in the filtrate. But when the soil is left in contact with the acetic acid for a period of three days, the same results are obtained because of the low dissociation of the acetic acid and thus lower rate of action.

Before discussing the importance of the potential acidity, a short review must be given of the influence of hydrogen-ion concentration on most cultivated plants.

When the pH value is over 9 or under 4, growth is inhibited so that only a few species are able to grow there without being severely injured.

Such results were obtained in culture experiments by Hoagland (10) and others (13). As all these workers have made their experiments with either solution or sand cultures and as the conditions in these media probably are not quite natural, the author undertook a similar work with soil.

The soil employed is garden soil from Java (table 7). Eight pots were filled with this soil and they were treated with different amounts of acid and alkali so that a series of soils was obtained whose pH values were whole numbers and ranged from 3 to 10. Table 3 shows the effect of this treatment on germination, stand after 2 months, average leaf surface after 14 days and 2 months, and the total leaf surface after 2 months. These results show a close resemblance to those obtained either in sand or in water cultures. It is evident that the optimum hydrogen-ion concentration for all plants investigated lies within a wide range.

Within this optimum range, we find a mass of irregularities in the growth of plants which depend upon the influence of the actual acidity.

The bacterial flora (7) of the soil plays a very great rôle in the nutrition balance and life of higher plants. So, for instance, we have the different nitrifying bacteria working in different pH zones.

Some of the plant pathogenes⁴ spend a part of their life cycle in the soil and are dependent on the hydrogen-ion concentration of the substrata; others are not, as is easily seen from table 4.

Probably the fauna of the soil also is strongly influenced by this factor as has been shown for earthworms (2).

The solubility of different salts is also dependent on the degree of acidity of the soil solution. For instance, iron phosphate and aluminum phosphate are precipitated at a pH value of 3 to 5. The same thing happens with other phosphates and calcium and magnesium salts, as is seen from the titrations by Hildebrand (9). In the case of aluminum salts a large amount of these in solution may cause a poisoning of plants, as is shown for rye and rice.

⁴ The strains were kindly furnished by Prof. Horne, Univ. of Cal.

TABLE 3
The influence of soil acidity on plant growth

SOIL REACTION	RATE OF GERMINATION	GERMINATION	LIVE PLANTS AFTER 2 MONTHS	AVERAGE LEAF SURFACE		TOTAL RELATIVE LEAF SURFACE AFTER 2 MONTHS
				14 days	2 months	
Bersim						
<i>pH</i>		<i>per cent</i>	<i>per cent</i>			
3	0.06	15	0	0	0	0
4	0.20	47	25	1.7	2.8	0.35
5	0.20	60	51	2.9	7.2	2.2
6	0.32	62	55	4.8	4.7	1.6
7	0.42	75	78	6.8	7.1	4.2
8	0.47	82	71	8.3	11.2	6.5
9	0.66	100	73	8.5	6.6	4.9
10	0.25	57	50	7.6	2.7	0.75
Barley						
3	0.13	65	72	21	39	18.3
4	0.23	95	71	27	36	24.1
5	0.18	97	66	29	53	33.4
6	0.29	95	100	29	63	59.8
7	0.25	100	90	30	67	60.3
8	0.31	97	74	34	65	46.8
9	0.31	100	93	32	80	74.4
10	0.26	100	54	30	38	20.5
Corn						
3	0.10	67	100	24	41	31.6
4	0.15	95	100	28	65	61.7
5	0.16	95	98	26	56	52.0
6	0.16	93	98	33	79	71.0
7	0.24	100	98	31	53	51.9
8	0.23	95	100	40	56	53.2
9	0.24	100	100	44	58	58.0
10	0.25	100	98	54	67	65.7
Cotton						
3	0.07	50	57	22	17	4.6
4	0.14	62	86	41	67	34.8
5	0.20	72	91	82	68	44.2
6	0.18	82	94	83	75	56.2
7	0.23	82	88	82	71	51.1
8	0.23	85	98	74	50	41.5
9	0.19	75	90	101	79	53.6
10	0.18	82	76	4	24	14.9

TABLE 3—Continued

SOIL REACTION	RATE OF GERMINATION	GERMINATION	LIVE PLANTS AFTER 2 MONTHS	AVERAGE LEAF SURFACE		TOTAL RELATIVE LEAF SURFACE AFTER 2 MONTHS
				14 days	2 months	
Wheat						
pH		per cent	per cent			
3	0.05	17	100	11	26	3.4
4	0.11	37	87	12	24	7.6
5	0.24	52	94	33	63	30.5
6	0.28	55	100	28	53	29.0
7	0.28	72	91	25	50	32.8
8	0.29	72	88	47	80	50.4
9	0.35	70	70	50	86	41.0
10	0.17	42	100	7	27	11.0

When working with different tropical and subtropical soils the author found a very good correlation in some cases between the fertility of the soil and the titration curve. When the soils showed a strong buffer effect,⁵ they were of good fertility; when they acted as weak buffers, their fertility was poor, (see tables 5-8).

Table 5 represent 16 tobacco soils from Sumatra. The rest are grouped around the four here given. Those acting as good buffers and more alkaline than pH 7 are resistant against the tobacco-wilt disease (*Slijmziekte*, *Bact. solanacearum*). The weak buffer soils, and those more acid than pH 7, however, are often devastated by this disease. In the weak buffer soils, the reaction is easily changed into the optimum field of bacterial growth.

The investigations of 20 rice soils (4) from Java are represented by two soils (in table 6), Soere and Rimboeloor. Here we find the same conditions as in the former case, probably we have to deal with a weakening of the rice plant and possibly with the effect of aluminum. Of great interest is that these two soils are from the same district and of the same origin, but afterwards

TABLE 4

Influence of hydrogen-ion concentration on viability of plant pathogens

NAME OF ORGANISM	INDEX OF VIABILITY AT DIFFERENT SOIL REACTIONS						
	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
<i>Bacterium citriputale</i>	0	2	8	10	10	10	5
<i>Botrytis cinerea</i> (potatoes).....		8	7	5	4	3	2
<i>Pythium</i> sp. (potatoes).....		10	10	10	10	5	10
<i>Sclerotium rolfsii</i> (Iris).....	8	8	9	9	10	10	10
<i>Polystictum versicolor</i>	0	10	10	10	10	6	6
<i>Bact. solanacearum</i> (tobacco).....	0	5	10	6	0		

⁵ By buffer effect is meant the ability to take up acids or alkalis without or but slightly changing the actual acidity.

differentiated by several factors. In the same table we find the result of a titration of a humus-rich garden soil and of a volcanic ash, taken fresh and stored for two years. It may be of interest to compare this young soil with the relatively old Demak soils.

The titration curves of some Egyptian (1) soils are found in table 7. Of these the Damanhour soil is exceedingly unfertile, the Nile suspension and the

TABLE 5
Effect of addition of acid or alkali upon the hydrogen-ion concentration of tobacco soils (Sumatra)

SOIL		TREATED WITH 0.1 N H ₂ SO ₄					TREATED WITH 0.1 N NaOH				
		cc.	pH								
Kaloecan Penang Black, good....	cc.	2.80	1.40	0.56	0.28	0.00	0.29	0.58	1.46	2.92	
	pH	4.0	5.0	7.0	7.2	7.2	7.4	7.6	8.4	9.5	
Songei Mentjirim Black, bad...	cc.	2.49	1.25	0.50	0.25	0.00	0.26	0.52	1.30	2.59	
	pH	2.5	3.5	4.5	5.5	7.0	7.5	8.0	>8.0	>8.0	
Toentongan Black, good.....	cc.	2.55	1.28	0.51	0.26	0.00	0.27	0.53	1.33	2.66	
	pH	4.0	5.0	6.0	6.8	7.0	7.2	7.5	8.0	>8.0	
Toentongan Red, bad.....	cc.	2.41	1.20	0.42	0.24	0.00	0.25	0.50	1.25	2.50	
	pH	2.0	3.0	4.0	5.0	6.7	7.2	8.0	>8.0	>8.0	

> This sign indicates "more than."

TABLE 6
Effect of addition of acid or alkali upon the hydrogen-ion concentration of Java soils

SOIL		TREATED WITH 0.1 N HCl					TREATED WITH 0.1 N NaOH				
		cc.	pH								
Rimboelcor Demak, good.....	cc.	2.33	1.17	0.47	0.23	0.00	0.14	0.27	0.68	1.37	
	pH	6.5	7.2	7.7	7.8	7.8	7.9	8.1	9.0	10.0	
Soere Demak, bad.....	cc.	2.44	1.22	0.49	0.24	0.00	0.14	0.28	0.71	1.42	
	pH	3.8	5.0	6.5	6.7	7.0	7.2	7.4	8.8	9.8	
Garden soil Buitenzorg, good	cc.	4.8	4.24	2.94	2.12	0.84	0.42	0.00	0.24	0.50	
	pH	4.5	6.5	6.8	7.0	7.2	7.3	7.3	7.6	7.9	
Volcanic ash Kediri.....	cc.	2.12	1.06	0.41	0.20	0.00	0.12				
	pH	2.6	3.5	4.0	4.5	7.0	9.5				

garden soil, however, are very fertile. In this case we see that the pH value of the Damanhour soil lies on the alkaline side of the growth limit. The sand is a soil type which is easily reclaimed, but also very easily destroyed by alkali. Also in these soils we see the same thing as in the case of the volcanic ash and the Demak soils. The Nile suspension has a comparatively weak buffer action when compared with the old garden soil and Damanhour soil.

Among the California soils the strongest buffer effect was shown by the garden soil.

The soils 1, 3 and 6 (used by Stewart (15)) are of the same soil type and show similar titration curves, whereas number 7 is of another type; here, however, 3 and 7 are bad and 1 and 6 good. In this case the pH value is at the neutral point and apparently the changes in reaction caused by the plants do not form any unfavorable conditions, whereas other factors, as the amounts of nutrients present are the chief factors of growth.

Of great interest are the soils from Ignacio near San Francisco. One of the samples, an extremely acid subsoil, probably represents the soil type before being worked and limed. The unlimed soil is thoroughly worked, but not limed and is now yielding a poor crop of beets; on the same field a part was limed resulting in an exceedingly good crop. The value of the soils is quite in

TABLE 7
Effect of addition of acid or alkali upon the hydrogen-ion concentration of Egyptian soils

SOIL USED		TREATED WITH 0.1 N HCl				TREATED WITH 0.1 N NaOH			
Garden soil Giza, good.	cc.	3.17	1.98	0.75	0.00	0.29	1.02	2.08	
	pH	7.2	7.4	7.5	7.6	8.0	9.5	11.0	
Damanhour, soil, bad.	cc.	0.00	0.31	0.72	1.15	1.56	2.15	3.71	5.4
	pH	11.00	10.0	9.0	8.7	8.4	8.1	7.6	7.3
Nile Suspension, Cairo.	cc.	1.77	0.93	0.11	0.44	0.20	0.00	0.23	0.47
	pH	3.0	6.5	7.0	7.2	7.4	7.4	7.5	7.8
Sand El-Munayer.	cc.	0.29	0.00	0.20	0.32	0.76		1.25	1.94
	pH	4.0	7.0	7.4	7.8	11		9.2	10.5

accordance with what has been said above on the correspondence between titration curve and soil fertility.

From the tables one sees that there is a correlation between the buffer action and the fertility of the soil. If the actual acidity of a soil lies within certain limits the buffer action of the soil is of great importance, so that strong buffer action is a good property; weak, a bad property. This action, however, is an indirect one. All soils are in a developing phase. The vegetation plays a great rôle on the one hand through the decomposing plant debris and root excretions and on the other hand through substances formed by the decomposition such as carbonic acid, etc. In arid climates the soil is more influenced by the formation of alkaline substances.

If there is, for instance, an acidifying process going on in the soil we may look at the process as a sort of a titration with an acid. A certain amount of acid substances is given off by the plant and in some soils we see a strong change caused by this action, in others the change is perhaps scarcely visible. The latter soils are the strong buffers, the former, weak. In this way the soil

reaction of the weak buffer soils is more easily changed to a range which is in some way injurious to the plant, than in the case with those having a strong buffer effect. Then the question arises how to improve the buffer effect of soil.

TABLE 8
Effect of addition of acid or alkali upon the hydrogen-ion concentration of California soils

SOIL USED		TREATED WITH 0.1 N H ₂ SO ₄				TREATED WITH 0.1 N NaOH				
1A.....	cc.	2.42	1.21	0.48	0.24	0.00	0.12	0.25	0.61	1.22
	pH	3.1	4.1	5.0	6.2	7.0	7.4	7.8	8.4	9.3
1B.....	cc.	2.29	1.15	0.45	0.23	0.00	0.11	0.23	0.58	1.17
	pH	3.3	4.5	5.4	5.9	7.0	7.4	7.8	8.1	9.0
3A.....	cc.	2.60	1.30	0.52	0.26	0.00	0.13	0.27	0.67	1.33
	pH	3.0	4.3	5.1	6.0	7.0	7.4	8.2	9.0	10.0
3B.....	cc.	2.25	1.12	0.45	0.23	0.00	0.12	0.24	0.57	1.14
	pH	3.3	4.8	5.8	6.2	7.0	7.4	7.8	8.4	9.5
6A.....	cc.	2.61	1.30	0.52	0.26	0.00	0.12	0.27	0.66	1.32
	pH	2.9	4.4	5.6	6.2	7.0	7.6	8.1	9.0	10.5
6B.....	cc.	2.35	1.17	0.47	0.24	0.00	0.12	0.25	0.60	1.19
	pH	3.2	4.8	5.9	6.4	7.0	7.5	7.8	8.3	9.7
7A.....	cc.	2.34	1.17	0.47	0.23	0.00	0.12	0.23	0.59	1.19
	pH	1.7	2.8	4.4	5.4	6.7	7.0	7.9	8.7	9.0
7B.....	cc.	2.16	1.08	0.43	0.22	0.00	0.11	0.22	0.55	1.10
	pH	2.0	3.0	4.6	5.4	6.7	7.0	7.7	8.7	9.5
Garden soil.....	cc.	4.44	2.22	1.11	0.44	0.22	0.00	0.05	0.11	0.57
	pH	2.5	4.8	5.2	6.2	7.0	7.2	7.3	7.3	7.4
									1.13	4.52
									8.0	12.0
Ignacio Hard, Sub-soil.....	cc.	3.04	1.52	0.61	0.30	0.0	0.16	0.31	0.78	1.55
	pH	2.3	3.0	4.0	4.8	5.1	5.8	6.1	6.7	8.2
Ignacio, Soft Limed, good.....	cc.	2.15	1.08	0.43	0.22	0.00	0.11	0.23	0.55	1.10
	pH	3.0	4.3	5.2	6.3	6.9	7.4	7.7	8.0	8.4

The nutrient salts of the soil are of very little importance as buffers as can be seen from table 8 where all "B" soils are unplanted and therefore rich in salts, and the "A" soils have been cropped for six years and are therefore rather exhausted.⁶ Liming only moves the reaction over towards the alkaline

⁶ In table 9 the titration of a modified Hoagland's solution is given. This represents a good soil solution. It can be seen that the titratable acidity is very weak when compared with that of the soils.

side and does not increase the buffer effect to any appreciable extent (as seen from the limed Ignacio soil).

It seems, considering Javanese and California garden soils as compared with the mineral soils from the same districts⁷ that good humus-manuring would improve the buffer curves in a relatively short time.

Another way is suggested by comparison of the old and new soils. Through weathering and decomposition the buffer effect is increased. This process can be accelerated by cultivation.

It seems as if it would be possible to ascertain the lime requirement of a soil by titration. By lime requirement, one means two things, partly the amount of lime required for "neutralizing" a soil and partly, in lime-poor soils, the amount required to fill the nutrition balance. The "neutralizing" lime only, is to be considered here.

TABLE 9
Effect of addition of acid or alkali upon the hydrogen-ion concentration of modified Hoagland's solution

	0.1 N HCl		0.1 N NaOH							
	0.03	0.01	0.00	0.08	0.22	0.57	0.77	0.88		
Cc. of acid or alkali added per gm. solution	3	4	5	6	7	8	9	10		
Resulting reaction of modified Hoagland's solution.										

A review of the literature shows that many methods have been used to determine soil acidity. There are three different types of these methods. First, the titration method in which only one actual pH determination is made, namely, the end point of the titration. Some use phenolphthalein, and others, other indicators.

Another type is that in which only a qualitative test with an arbitrarily chosen method is made.

Christensen used a biological method in which the growth of *Azotobacter* was the indicator.

What is done in all these cases and what it is aimed to do is to change the reaction of the soil to a certain point. Why not do it by titration with a strong but diluted acid (or alkali) in order to get the reaction as quickly as possible and then locate the different points on the pH scale. By using this method the arbitrariness would be reduced to a minimum and one would obtain a universal and simple method for the determination of the lime requirement.

SUMMARY

The potential acidity of the soil or the buffer action is an important and nearly overlooked factor. It has been found that in some cases there is a good correlation between the type of titration curve and fertility. A strong buffer

⁷ A good suggestion in this work would be to select a certain green manure crop of which the manure is as near neutral as possible in order to avoid too much liming.

action means a good soil, a weak one a bad or easily changed soil, provided the reaction of the soil lies within certain limits. Humus-manuring and cultivation are the two factors for increasing the buffer effect.

The titration of soils may be used for determination of the lime requirement.

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