On the Catalytic Action of Soils.

By

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Introduction.

By soil-catalysis is meant the power of soil to decompose hydrogen peroxide with the liberation of oxygen.

Since it is recognized at the present day that soil is not only the reservoir of plant foods but also is a laboratory of many complex physical, chemical and biological changes, which influence soil-fertility directly and indirectly, the study of soil must also be extended to those above mentioned changes in it.

Investigations on the physical, chemical and biological changes in soil, have been carried out from the above point of view; and among them, the study of soil-catalysis is to be numbered.

The present writer had an opportunity to make some experiments on soil-catalysis, and obtained results which may not have any direct connection with soil-fertilty; but he feels that they throw some light upon the nature of soil-particles.

Literature.

J. KÖNIG, J. HASENBÄUMER and E. COPPENRATH[1] tested soil-catalysis, and found that it is rendered very small by treatment with mercuric chloride, chloroform, iodine and prussic acid or by heating soil, and accordingly, they attributed this power to the action of catalase and of inorganic colloidal substances in soil.

D. W. WAY and P. L. GILE[2] investigated soil-catalysis, and concluded that the action is mainly due to the presence of bacteria and enzyme, and also to colloidal substances, of organic and inorganic natures, in soil.

They confirmed the fact that the action is much influenced by 1) The

1) KÖNIG, J., HASENBÄUMER, J. and COPPENRATH, E., Landw. vers. stat. 63 (1906) No. 5—6.
2) WAY, D. W. and GILE, P. L., Porto Rico, Stat. Circ. 9, p. 3—13 abst. in E. S. R. 21 (1909) p. 220.

quantity of catalase in soil.   2) The concentration and the quantity of hydrogen peroxide applied.   3) The reaction of soil.   4) The temperature applied.   5) The presence or absence of agitation.

They found also that high temperature and carbon bisulphide etc. have depressing effect on soil-catalysis; but, that this is not the case with manures.

M. X. Sullivan and F. R. Reid[1] denied the existence of catalase and attributed soil-catalysis to the action of inorganic and organic substances in soil and recognized the close relation between the catalytic power of soil and its fertility.

H. Kappen[2] came to almost the same conclusion as that which Sullivan and Reid had already obtained.

As will be seen from the above reports, the results of the investigations on the nature of soil-catalysis and the substances causing it are not always consistent and thus it becomes necessary to repeat experiments in order to reach a definite conclusion on the subject.

Experimental.

1. Relation between soil-catalysis and the physical condition of soil-particles.

Exp. 1.   In June 1921, two series of twenty Wagner's pots, filled with twenty different soils, were prepared.

One series of pots, was manured with sulphate of ammonia, disodium phosphate and sulphate of potash at the rate of eight Kans[3] of nitrogen, six of phosphoric acid and six of potash per Tan[4] while the other twenty pots were left unmanured.

All pots were planted with paddy rice plant in the usual way.

After one week of planting, sample were collected from each pot, air-dried, sieved gravels out and used for experiment.

In October of the same year, at the harvest, sampling was made from each pot in exactly the same way as above.

In November, the previously manured pots, only, were manured with the same composition and rate, and barley was sown in all pots.

The sampling was carried out in exactly the same way as above from all pots.

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1) Sullivan, M, X. and Reid, F. R.,   Bul. 86, Bur. of soil.   U. S. dept. agr. (1912) p. 31.
2) Kappen, H.,   Fühlings landw. ztg. 62 (1913) s. 377—392.
3) 1 Kan = 3.75 kg.
4) 1 Tan = 1/4.06 acre.

With these samples, determination of catalytic power was made by adding 100 c.c. of 1% hydrogen peroxide neutralized[1] to each 10 grs. soil, shaking one hour, titrating hydrogen peroxide undecomposed with $\frac{N}{10}$KMnO$_4$ solution and calculating the difference of titration value between control and the sample.

The following table of results shows the number[3] of c.c. of $\frac{N}{10}$KMnO$_4$ solution corresponding to the quantity of hydrogen peroxide decomposed by 10 grs. soil.

Soil No.	June after first manuring and before planting paddy rice.		October after harvesting paddy rice.		November after 2nd manuring.	
	Manured	Unmanured	manured	Unmanured	Manured	Unmanured
1	100.60	110.00	101.90	111.40	93.50	100.50
2	86.97	100.40	105.20	107.50	83.00	97.00
3	65.26	98.10	98.30	101.40	62.00	92.00
4	74.06	110.20	103.60	108.30	72.00	103.50
5	89.03	124.00	106.50	114.10	82.50	101.50
6	83.02	98.00	110.10	111.70	85.50	104.00
7	93.14	102.50	102.30	112.80	89.00	108.00
8	81.67	97.70	105.50	117.70	80.50	104.00
9	79.33	116.00	113.00	106.00	79.00	94.50
10	89.04	99.00	119.00	108.00	88.50	101.50
11	68.09	102.80	110.50	108.80	60.00	102.50
12	85.77	115.30	111.50	118.40	88.60	106.50
13	73.07	100.20	104.30	110.60	71.50	96.00
14	92.39	121.10	106.60	118.20	94.00	101.50
15	91.76	120.50	110.10	119.50	87.00	98.00
16	72.90	108.30	107.70	115.30	72.50	96.00
17	91.18	125.20	109.70	122.70	86.00	112.50
18	84.42	119.60	118.00	125.00	97.50	112.50
19	83.96	118.70	113.10	120.70	86.50	113.00
20	95.81	121.30	109.10	118.30	94.00	109.00

1) In all experiments throughout this investigation, the writer used always neutralized hydrogen peroxide.

2) In Control, 100 cc. of 1% hydrogen peroxide solution only was shaken for one hour. When some addition was made hydrogen peroxide added with reagent, was shaken as control. This calculation was same in all experiments described under

3) In all following experiments, the quantity of the decomposed hydrogen peroxide was expressed in the same way.

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From the above table, it is to be seen that the catalytic power of the ma-
nured soil is always smaller than that of the unmanured at the first manuring;
the difference disappears at the harvest, but reappears after the second ma-
nuring.

Exp. 2. In order to discover the reason for the above changes of the
catalytic action of soils during various seasons, the writer at first tested the
concentration of the water-extract of each sample by measuring the electric
conductivity and calculated the concentration by comparing it with that of $\frac{N}{50}$
potassium chloride solution.

The result is given in the next table,[1] which shows that the difference
between the concentrations of the water-extract[2] of the manured and unma-
nured soils is not distinct at the harvesting time, but after the second manur-
ing, the concentration of the former is markedly larger than that of the latter.

Soil No.	Date of sampling			
	October (after harvesting paddy rice)		November (after second manuring)	
	Manured (%)	Unmanured (%)	Manured (%)	Unmanured (%)
1	0.0102	0.0096	0.0522	0.0140
2	0.0286	0.0278	0.0606	0.0133
3	0.0173	0.0145	0.0505	0.0133
4	0.0082	0.0089	0.0577	0.0136
5	0.0062	0.0067	0.0562	0.0186
6	0.0162	0.0195	0.0604	0.0174
7	0.0187	0.0069	0.0494	0.0128
8	0.0124	0.0189	0.0832	0.0117
9	0.0129	0.0163	0.0680	0.0194
10	0.0383	0.0284	0.0626	0.0238
11	0.0287	0.0272	0.0502	0.0203
12	0.0169	0.0145	0.0875	0.0112
13	0.0182	0.0130	0.0793	0.0153
14	0.0135	0.0100	0.0835	0.0113
15	0.0117	0.0284	0.0650	0.0106
16	0.0181	0.0147	0.0688	0.0125
17	0.0175	0.0223	0.0579	0.0197
18	0.0196	0.0147	0.0655	0.0178
19	0.0129	0.0117	0.0694	0.0178
20	0.0133	0.0171	0.0677	0.0166

R. O. E. DAVIS[3] reported that soluble salts have strong coagulating action
on soil-particles especially on the finest clayey part.

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1) The result is expessed in terms of percentage composition of potassium chloride.
2) Water extract was prepared by shaking 10 grs. of soil with 100 c c. of distilled water for one
hour and filtering.
3) DAVIS, R. O. E., Bul. 82, (1912) Bur. of soil. U. S. dept. agr.

D. R. HOAGLAND and J. C. MARTIN's[1] experiments led them to state that soluble salts in soil cause soil-particles to coagulate and the diminution of soil-solution by plant-growth results in the increase of the colloidal part[2] in soil.

In order to determine the quantity of the colloidal part of soil, the writer shook 30 grs. of sample with 60 c.c. of water for one hour and stood at room temperature for 48 hrs.

Pipetting off the liquid part and dialyzing it throughly, it was evaporated into dryness and the residue weighed.[3]

The following results were calculated for 100 grs. soil.

Soil No.	June (after first manuring and before planting paddy rice)		October (after harvesting paddy rice)		November (after second manuring)	
	Manured %	Unmanured %	Manured %	Unmanured %	Manured %	Unmanured %
1	0.0393	0.3512	0.2590	0.3161	0.0593	0.3005
2	0.0621	0.2513	0.2511	0.2003	0.0664	0.2170
3	0.0125	0.1517	0.1662	0.1491	0.0125	0.1491
4	0.0352	0.1489	0.1750	0.1472	0.0383	0.1804
5	0.0425	0.1025	0.1272	0.1422	0.0615	0.1384
6	0.0526	0.4897	0.3191	0.4193	0.0622	0.3697
7	0.0623	0.3235	0.2578	0.3254	0.0624	0.3839
8	0.0679	0.1150	0.1281	0.1294	0.0685	0.1231
9	0.0411	0.1435	0.1342	0.1895	0.0300	0.1822
10	0.0256	0.1230	0.1051	0.1130	0.0244	0.0857
11	0.0257	0.3571	0.3912	0.3356	0.0230	0.4532
12	0.0289	0.1251	0.0857	0.0841	0.0267	0.1320
13	0.0471	0.3453	0.2753	0.3852	0.0544	0.2872
14	0.0256	0.2507	0.2447	0.2209	0.0127	0.3351
15	0.0219	0.4059	0.3512	0.4703	0.0077	0.3717
16	0.0315	0.1351	0.1424	0.1145	0.0392	0.1254
17	0.0578	0.1528	0.2331	0.1620	0.0545	0.1274
18	0.0319	0.3019	0.2293	0.2938	0.0285	0.1785
19	0.0521	0.2412	0.1897	0.2021	0.0463	0.2305
20	0.0159	0.1251	0.1837	0.1684	0.0338	0.1458

Hence, it will be seen from the above table that the quantity of particles in suspension or of colloidal part is in the reverse ratio with the concentration of the soil-extract and in intimate relation with the catalytic action.

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1) HOAGLAND, D. R. and MARTIN, J. C.,   Jour. agr. res. Vol. 20, (1920) No. 5, p. 397—404.

2) Here " colloidal part " means " suspension."

3) See, WOLCOFF, soil science, Vol. 3, No. 5 (1917) p. 424.

Exp. 3. To each 10 grs. of sample collected from unmanured pots in November, 1 gr. of sodium chloride was added, and the whole was shaken for one hour with 100 c.c. of 1% hydrogen peroxide.

The quantity of hydrogen peroxide decomposed was as follows;

Soil No.	Sample from unmanured pot in November.		Soil No.	Sample from unmanured pot in November.	
	No addition	Added		No additioe	Added
1	100.5	63.0	10	101.5	68.5
2	97.0	63.5	11	102.5	68.0
3	92.0	42.7	12	106.5	74.5
6	104.0	74.5	13	96.0	48.0
7	108.0	72.0	14	101.5	68.0
8	104.0	65.0	16	96.0	54.5
9	94.5	66.0	18	112.5	95.0

The above result shows that the unmanured soil which showed greater activity on hydrogen peroxide than the manured soil, when it has previously received the addition of sodium chloride and accordingly, the coagulation of soil particles, acts in almost the same manner as the manured soil.

Exp. 4. Considering the results of Exp. 1—3, it is clear to be seen that soil-catalysis has a close relation to the quantity of colloidal substances contained in soil and this is more completely confirmed by the following experiment.

With chloride of calcium, barium, sodium and potassium which are known to act on soil particles so as to coagulate them, their effect on soil-catalysis was tested in exactly the same way as shown in the preceeding experiment[1] and found that the above salts inhibit catalysis distinctly as follows[2];

Sample	$BaCl_2$	$CaCl_2$	KCl	NaCl	Control (H_2O)
C	24.0	19.0	12.0	26.0	39.0
D	75.6	73.6	78.6	94.0	96.4
E	16.6	7.6	7.6	11.4	22.4
F	16.0	10.4	13.0	28.4	30.1
I	20.5	8.8	26.0	43.0	56.0
J	15.0	17.0	14.4	14.0	24.0
K	22.2	21.0	27.0	26.0	30.0
L	28.0	29.4	19.0	29.6	40.0
M	0.6	0	10.6	12.5	17.5
N	26.0	17.5	42.0	49.0	38.4
O	49.4	53.4	58.0	63.0	71.0
P	32.0	36.0	40.6	50.0	61.0

1) 10 grs. of soil was shaken for one hour with 50 c.c. of N/10 salt mentioned and the whole was shaken again for one hour with 50 c.c. of 0.4% hydrogen peroxide and the filtrate was titrated.

2) The quantity of hydrogen peroxide decomposed.

With the following potassium-salt-solutions, the same experiment[1] as the preceeding one, was conducted in order to test the effect of these salts on soil-catalysis and the result obtained is shown in the next table.[2]

Soil	Citrate	Tartarate	Acetate	Water	Sulphate	Chlorate	Chloride	Nitrate
A	55.0	36.6	40.0	35.5	21.0	16.0	15.0	14.0
B	93 0	76.0	62.0	73.0	60.0	38.0	47.0	40.0
C	53.6	44.0	57.6	40.4	32.0	22.0	24.6	23.6
D	114.0	109.6	107.0	98.4	107.4	62.0	95.6	61.6
E	68.0	47.0	37.4	25.6	37.0	18.4	14.4	12.6
F	44.0	44.0	30.7	32.0	37.0	22.0	33.0	37.0
G	55.0	52.0	52.7	50.6	49.6	34.4	40.0	37.0
H	89.6	76.0	76.0	54.4	58.0	17.6	42.4	35.0
I	71.6	61.4	69.0	66.0	62.6	59.6	58.4	64.0
J	43.0	38.0	24.6	22.4	13.4	13.4	12.6	10.6
K	61.0	39.6	30.0	24.0	27.0	16.0	21.6	16.6
L	40.4	39.0	34.4	36.6	37.0	21.0	31.0	24.6
M	69.6	40.0	20.6	19.0	15.0	11.0	12.4	10.6
N	81.6	64.4	35.6	36.0	34.4	34.0	51.0	35.6

The above result, was arranged in the order of the magnitude of the decomposed hydrogen peroxide as follows;

Soil	Catalytic power
A	citrate > acetate > tartarate > H_2O > sulphate > chloride > chlorate > nitrate
B	citrate > tartarate > H_2O > acetate > sulphate > chloride > nitrate > chlorate
C	acetate > citrate > tartarate > H_2O > sulphate > chloride > nitrate > chlorate
D	citrate > tartarate > sulphate > acetate > H_2O > chloride > chlorate > nitrate
E	citrate > tartarate > acetate > sulphate > H_2O > chlorate > chloride > nitrate
F	citrate > tartarate > sulphate > nitrate > chloride > H_2O > acetate > chlorate
G	citrate > acetate > tartarate > H_2O > sulphate > chloride > nitrate > chlorate
H	citrate > tartarate > acetate > sulphate > H_2O > chloride > nitrate > chlorate
I	citrate > acetate > H_2O > nitrate > salphate > tartarate > chlorate > chloride
J	citrate > tartarate > acetate > sulphate > H_2O > chloride > nitrate > chlorate
K	citrate > tartarate > acetate > sulphate > H_2O > chloride > nitrate > chlorate
L	citrate > tartarate > sulphate > H_2O > acetate > chloride > nitrate > chlorate
M	citrate > tartarate > acetate > H_2O > sulphate > chloride > chlorate > nitrate
N	citrate > tartarate > chloride > H_2O > acetate > nitrate > sulphate > chlorate

1) To 10 grs. of soil, was added 50 c.c. of N/10 soil, shaken for one hour and taken tested the catalytic power after being shaken the whole with 50 c.c. of 0.4% H_2O_2 for one hour.
2) The quantity of hydrogen peroxide decomposed.

From the above result, it is to be seen that, on the whole, inorganic salts inhibit the catalytic action of soil and organic salts, especially citrate and tartarate, accelerate it distinctly.

In the above experiment, the writer observed the fact that the shaken sample added by inorganic salt is easily filtrable and the one added by organic salt, especially by citrate or tartarate, is very difficultly filtrable.

Although the above fact may indicate that the different effect of inorganic and organic salt upon soil-catalysis, is to be due to the different physical effect of these salts upon soil particles, the writer made an experiment in order to determine the coagulating and peptizing effect upon soil-particles of potassium chloride (as a representative of the above inorganic salts) and potassium citrate (as a reprecentative of the above organic salts) by measuring the quantity of particles in suspension.

In this experiment, 10 grs. of soil was shaken for one hour with 100 c.c. of $\frac{N}{20}$ salt solution, stood for 48 hours, dialized, evaporated and weighed the residue.

The result is as follows ;

Soil		A	B	C	D	E	I	J	K	L	M	N
KCl	%	0	0	0	0	0	0	0	0	0	0	0
K-citrate	%	0.160	1.960	2.240	1.000	6.337	0.600	2.668	0.072	0.050	16.428	0.520
H₂O	%	0.024	0.124	0.284	0.052	trace	trace	0	0	0	0	0

The above table shows that potassium chloride which showed inhibiting effect, coagulates soil-particles and potassium citrate which had acceleratory effect, peptizes soil particles remarkably.

O. Schreiner and M. X. Sullivan[1] reported that oxy-acid like citric and tartaric acid, accelerates oxydizing action of soil and they attributed this acceleration to the special chemical construction of these acids.

In case of soil-catalysis, the present writer found the accelerating power of tartarate and citrate of potash to exist, as stated above, and he attributed this acceleration to the peptizing action of these salts on soil-particles, but it is not certain whether this is or is not due to the special chemical construction of the molicules of these acids.

In order to determine this, the present writer added 50 c.c. of $\frac{N}{50}$ tartaric or citric acid solution to 10 grs. soil, shook the whole for one hour and then determination of the quantity of hydrogen peroxide decomposed after the shaken sample had been shaken again for one hour with 50 c.c. of 0.4% hydrogen peroxide, was carried out.

1) Schreiner, O. and Sullivan, M. X., Bul. 73, Bur. of soil. U. S. dept. agr.

The result was as follows;

Soil	A	B	C	D	E	F
Control (water)	34.0	67.0	40.4	95 4	28.5	31.0
Citric acid	15.4	2{.4	14.4	46.0	23.5	27.0
Tartaric acid	30.4	26.0	20.4	54.0	26.0	29.0

The above table shows that citric and tartaric acids have distinct in- hibitory action upon soil-catalysis.

The soil shaken with citric or tartaric acid solution is distinctly coagulated.

The above fact proves that the acceleratory action of citrate and tartarate is not due to their special chemical construction but mainly due to their pep- tizing effect upon soil-particles.

By the results obtained in Exp. 1—3, the present writer confirmed the fact that the treatment which causes to cougulate soil-particles, makes soil- catalysis smaller and that which peptizes soil-particles, acts in just the reverse way and inclines to conclude that the physical condition of soil-particles is an important factor in soil-catalysis and that the change in the catalytic power of soil by manuring with mineral fertilizers and cropping, as has been already recorded, is mainly due to the change in the physical condition of the soil- particles as the result of the change of the salt content of soil by manuring and plant-growth.

2. Effect of chemical soil-constituents on soil-catalysis.

Although the present writer inclines to conclude that the physical con- dition of soil-particles greatly influences soil-catalysis, there is no reason to consider as unimportant the effect of the chemical nature of soil on its cata- lytic activity.

As will be quoted below, while special soil constituent has remarkable catalytic power, other constituent has slight action or none at all on hydrogen peroxide.

This compelled the writer to investigate the nature of soil constituents to which soil-catalysis is mainly due.

J. KÖNIG, J. HASENBÄUMER and E. COPPENRATH[1] tested the catalytic power of manganese oxide, ferric oxide and aluminium oxide etc. and found that all of sesquioxides tested showed the power to decompose hydrogen peroxide ; monoxide and silicic acid ignited do not show any such power and hydro- xides, very slight activity.

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1) KÖNIG, J., HASENBÄUMER, J. und COPPENRATH, E., Landw. Vers. Stat. Bd. 66 (1907) s. 422.

Among the sesquioxides, manganese sesquioxide showed the greatest power and accordingly they concluded that there must exist close relation between manganese content and soil-catalysis.

A considerable catalytic power was found in ignited calcareous soil; and this may be attributed to the alkaline reaction due to calcium oxide resulting by ignition from calcium carbonate in soil.

D. W. WAY and P. L. GILE[1] reported that soil-reaction is an important factor in soil-catalysis.

M. X. SULLIVAN and R. E. REID[2] experimented on the increase of soil-catalysis by liming but did not determine this cause.

Experiment was also made on soil-humus and its action on hydrogen peroxide was found but no quantitative relation between humus content of soil and soil-catalysis could be observed.

H. KAPPEN[3] found that alkaline reaction of soil is an important factor in soil-catalysis.

The present writer made several experiments in the same line as quoted above and the result is now given in the following.

1) Catalytic action of humus substance.

Exp. 1. Humus extract was prepared by treating black soil with 0.1% sodium hydroxide solution.

The extract obtained was divided into two parts.

With one part, humus sol was made by dialyzing the extract in distilled water until no alkaline reaction is observed in the dialysate.

The sol obtained contained 0.13% of humus.

With the other part, humus gel was precipitated by acidifing the extract with hydrochloric acid and washed it with distilled water until no more chloride is recognized in the washing.

Taking 15 c.c. of the above sol and adding 10 c.c. of salt solution or acid or alkaline solution shown in the following table to it, it was then shaken for one hour with 25 c.c. of 0.4% hydrogen peroxide and the quantity of hydrogen peroxide decomposed was determined as follows;

Solution added[4]	K-citrate	K-tartarate	K-ch oride	Calcium chloride	H_2O	HCl	HONa
Hydrogen peroxide decomposed	12.5	11.0	9.0	7.0	10.0	0	15.0

1) WAY, D. W. and GILE, P. L., Porto Rico. stat. circ. 9. p. 3—13, abs. E. S. R. 21 (1909) p. 220.

2) SULLIVAN, M. X. and REID, R. E., Bul. 85 (1912) Bur. of soil, U. S. dept. agr.

3) KAPPEN, H., Landw. Ztg. Fühlings. 62, s. 377—392.

4) Salt-solution is 1/10 N. and acid and alkali solution are 1/50 N. respectively.

Exp. 2. 1 gr. of humus gel, yet moisted, was shaken with 50 c.c. of 0.2% hydrogen peroxide for one hour.

It was found that 2 c.c. of hydrogen peroxide was decomposed.

Exp. 3. Humus gel was dried in a steam bath, and powdered; then, taking 0.005 gr, its catalytic power was tested by conducting the experiment[1] in exactly the same manner as in Exp. 1.

The result is shown in the following table.

Solution added	K-citrate	K-chloride	Ca-chloride	H_2O	HCl	HONa
Hydrogen peroxide decomposed	2.0	o	o	1.0	o	0.5

From the results obtained in Exp. 1—3, it is seen that humus, both in forms of sol and gel, even in dried gel, decomposes hydrogen peroxide and that this power decreases much from sol-form to gel-form and lastly to dried gel, and that the effect of salt, acid and alkali-solution is almost the same as observed in the case of soil.

In order to find out whether there exists any correlation between humus content of soil and soil-catalysis, the writer determined both quantities as in usual way and compared them, as in the following table.

Soil No.[2]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Hydrogen peroxide decomposed	47.0	89.3	67.0	75.8	43.3	28.0	62.8	83.8	48.0	67.8	64.5	58.0	8.5	72.0	59.5	63.0	61.0
Order of the above	8	1	5	3	9	10	6	2	7	4	2	6	7	1	5	3	4
Humus content	1.00	trace	1.65	0	0	1.60	2.20	10.20	5.20	1.20	0.36	0.80	trace	5.12	0.60	very trace	1.80
Order of the above	7	8	4	9	10	5	2	1	2	6	5	3	6	1	4	7	2

From the above table, it is to be seen that some relation between the two quanties is established but no definite one is to be observed.

2) Catalytic action of silicic acid and silicates.

J. Könıg, J. Hasenbäumer and E. Coppenrath[3] reported that the soil extracted with hot hydrochloric acid loses its catalytic power to a remarkable degree, or even completely and that sea-sand, kaolin, albite, silicic oxide and potash feldspar decompose hydrogen peroxide to a very small extent.

From a consideration of this, the present writer supposes the action of

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1) In this case, volume of N/50 salt or acid or alkali-solution is 25 c.c. respectively.

2) In case of samples No. 1 to 10, each 10 grs. were shaken with 50 c.c. of 0.4% hydrogen peroxide for one hour, and in case of No. 11 to 17, each 10 grs. were shaken with 50 c.c. of 0.2% hydrogen peroxide for the same length of time.

3) König, J., Hasenbäumer, J. and Coppenrath, E., Landw. Vers. Stat. 63 (1906) s. 471.

silicic acid and silicate on hydrogen peroxide to be very slight, and this he confirmed in the following experiments.

Exp. 1. 1 gr. of each calcium silicate, aluminium silicate, kaolin, quartz sand and 0.1 gr. of silicic acid respectively, were shaken for one hour with 25 c.c. of salt[1] or acid or alkali-solution shown in the following table and then the catalytic power tested in the way as described in case of humus-gel.

The result given in the following table shows that none of the materials tested in this experiment shows catalytic action excepting calcium silicate.

Sample	K-citrate	K-tartarate	K-chloride	Ca-chloride	H_2O	HCl	HONa
Ca-silicate	4.5	9.8	5.5	6.3	17.0	1.0	4.5
Al-silicate	—	0	0	0	0		9.5
Silicic acid	0	0.8	0	0	0	0	—
Quarz-sand	0	0	0	0	0	0	—
Kaolin	0	0	0	0	0		28.0

The action of calcium silicate seems to be due to its alkaline reaction and not to silicate itself as will be experimented in the succeeding chapter.

Exp. 2. With silicic-acid-sol prepared with water glass solution and concentrated hydrochloric acid, the writer found no action.

From these two experiments, the writer does not hesitate to conclude that silicic acid, silicic oxide and silicate in soil have no distinct effect on soil-catalysis.

3) Catalytic action of aluminium oxide and silicate.

J. König, J. Hasembäumer and E. Coppenrath[2] have already experimented with oxide, hydroxide and silicate of alumina and found that aluminium hydroxide alone decomposes hydrogen peroxide only in a slight degree.

The present writer made also some experiments on aluminium oxide, silicate and kaolin and found catalytic action in none of them.

4) Catalytic action of oxide, hydroxide and
phosphate of ferric-iron.

The catalytic action of oxide and hydroxide of ferric-iron has been reported by J. König, J. Hasenbäumer and E. Coppenrath.[3]

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1) Salt is 1/10 N. and acid and alkali-solution are 1/50 N. respectively.

2) and 3) König, J., Hasenbäumer, J. and Coppenrath, E., Landw. Vers. Stat. 64, (1907), s. 422.

The present writer also proved this in the following experiments.

Exp. 1. Ferric-oxide-sol containing 0.0194% Fe was prepared.

To 10 c.c. of this was added 25 c.c. of the following salts,[1] or acid[2] or alkali-solution[4] and 5 c.c. of distilled water, mixed well, and then the quantity of hydrogen peroxide decomposed was tested, after being shaken the whole with 25 c.c. of 0.4% peroxide solution for one hour.

The result is as follows;

	H_2O	K-citrate	K-tartarate	K-acetate	KCl	$KClO_3$	KNO_3	SO_4K_2	ClNa	Cl_2Ca	Cl_2Ba	HCl	HONa
Hydrogen peroxide decomposed	7.3	6.5	5.5	9.7	4.5	7.0	7.2	6.0	4.5	4.0	5.0	1.5	7.3

Exp. 2. To each 1 gr. of bog-iron-ore, limonite, ferric oxide, hydroxide, and phosphate, was added each 25 c.c. of the following salts or acid or alkali-solution,[3] shaken one hour and the catalytic power was determined in the usual way with the result of following table.

	K-citrate	K-tartarate	K-chloride	Ca-chloride	H_2O	HCl	HONa
Bog-iron-ore	35.5	39.0	30.2	22.0	36.8	2.5	all decomposed
Limonite	23.5	26.0	22.0	9.5	20.8	3.0	28.5
Ferric oxide	48.7	46.5	45.0	42.8	46.3	20.5	all decomposed
Ferric hydroxide	53.2	46.7	47.5	46.0	48.8	31.2	„ „
Ferric phosphate	30.0	—	24.0	8.5	26.3	3.0	„ „

From the results of Exp. 1—3, it is clear that oxide (sol and gel), hydroxide and phosphate of ferric-iron decompose hydrogen peroxide to a remarkable extent and that the effect of reagents added was almost the same as in case of soil with a few exceptional cases.

Ferric chloride and sulphate solution in concentration of 0.0063—0.025% have not any power to decompose hydrogen peroxide.

5) Catalytic action of oxide and phosphate of manganese.

That manganese oxide is able to decompose hydrogen peroxide, has been already reported by J. KÖNIG, J. HASENBÄUMER and E. COPPENRATH,[4]

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1) 1/10 normal.

2) 1/50 normal.

3) Dilution is the same as in Exp. 1.

4) KÖNIG, J., HASENBÄUMER, J. and COPPENRATH, E., Landw. vers. stat. Bd. 66, (1907), s. 422.

and M. X. SULLIVAN and R. E. REID[1] as has been mentioned in the preceeding chapter.

The present writer made also some experiments on this.

Exp. 1. To 15 c.c. of manganese-oxide-sol,[2] prepared with Rochelle salt, sodium hydroxide and hydrogen peroxide and dialized, was added 10 c.c. of the following salts or acid or alkali-solution (same dilution as in the preceeding experiment) and the quantity of hydrogen peroxide decomposed was measured after being shaken with 25 c.c. of 0.4% hydrogen peroxide for one hour, with the following result.

H_2O	K-citrate	K-tartarate	K-acetate	SO_4K_2	KCl	NO_3K	ClO_3K	ClNa	Cl_2Ca	Cl_2Ba	HCl	NaOH
44.3	48.5	48.5	45.7	46.7	46.0	46.5	44.2	45.0	44.0	43.7	5.5	all decomposed

Exp. 2. With 1 gr. of each manganese dioxide, psilomelaen, pyrolusite and 0.2 gr. of manganese phosphate was made the same experiment as in case of ferric oxide and hydroxide etc.

The result is as follows;

	K-citrate	K-tartarate	KCl	$CaCl_2$	H_2O	HCl	HONa
Manganese dioxide	all decomposed	all decomposed	all decomposed	all decomposed	all decomposed	all decomposed	all decomposed
Psilomelaen	„ „	49.0	45.2	36.0	47.8	41.0	„ „
Pysolusite	„ „	48.5	46.0	38.5	49.8	39.0	„ „
Manganese phosphate	29.0	—	13.5	5.0	10.5	3.0	„ „

From the results of Exp. 1 and 2, it is seen that manganese oxide, both in forms of sol and gel, manganese dioxide and phosphate decompose hydrogen peroxide to a remarkable degree.

The effect of peptizing and coagulating agents is almost the same as in the experiments with soil, humus and ferric oxide, excepting a few cases.

Exp. 3. Comparing the catalytic power of oxide and phosphate of manganese and ferric-iron as will be seen in the next table, it is seen that manganese compound has always greater activity on hydrogen peroxide than that of corresponding ferric compound.

1) SULLIVAN, M. X. and REID, R. E., Bul. 58, (1912), Bur. of soils, U. S. dept. agr.
2) This sol contains 0.033% MnO.

	Hydrogen peroxide decomposed.
{ Ferric oxide (1 gr.)	46.3
{ Manganese dioxide (1 gr.)	>53.5
{ Ferric phosphate (0.5 gr.)	26.3
{ Manganese phosphate (0.2 gr.)	10.5
{ Ferric-oxide-sol (0.0019 gr.)	7.3
{ Manganese-oxide-sol (0.005 gr.)	44.0

Exp. 4. The experiment made with soluble manganese salts (chloride and sulphate in the same dilution as in case of ferric salts) shows no positive result as has been observed also in the case of ferric salts.

Exp. 5. Although it was observed by the experiments already mentioned, that peptizing agent causes the increase of the action of ferric-iron and manganese on hydrogen peroxide and that coagulating agent does in the reverse way, with a few exceptional cases, the present writer made one more experiment regarding this point, as follows;

Powder of manganese dioxide and ferric oxide was sieved into several grades of sizes as shown in the next table, and using 1 gr. of each sample, the catalytic power was tested as in the usual way.[1]

The result is given in the following table which shows that, the smaller the size, the greater the activity of particles.

Diameter of particles	2—1 m.m.	1—0.5 m.m.	0.5—0.25 m.m.	10.25 m.m.
Bog-iron ore	trace	4.0	17.0	28.6
Limonite	"	2.2	15.0	24.2
Psilomelaen	8.7	16.5	63.0	73.0
Pysolusite	23.2	34 0	80.0	92.0

Exp. 6. Regarding the quantitative relation between the content of iron and manganese of soil and soil-catalysis,[2] the writer could not find any definite relation as shown in the following table, but it does not prove the non-existence of effect of iron and manganese on soil-catalysis, since soil-catalysis is the result of many complex factors in soil; and from the consideration of the experimental results mentioned above, it is reasonably concluded that manganese and iron in soil are the main substances causing soil to decompose hydrogen peroxide.

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1) Shaking for one hour with 50 c.c. of 0.4% hydrogen peroxide.
2) The method determing catalytic power of the sample is the same as recorded in the preceeding experiment.

Soil No.	1	2	3	4	5	6	7	8
Hydrogen peroxide decomposed	47.0	89.3	67.0	75.8	43.3	28.0	62.8	83.8
Order of the above	8	1	5	3	9	10	6	2
Content of iron (Fe) %	1.369	1.174	1.191	2.582	1.500	0.971	1.321	2.720
Order of the above	6	9	8	2	5	10	7	1
Content of manganese (MnO) %	0.0124	0.0071	0.0055	0.0040	0.0075	0.0095	0.0124	0.0130
Order of the above	4	8	9	10	7	6	5	3

Soil No.	9	10	11	12	13	14	15	16	17
Hydrogen peroxide docomposed	48.0	67.8	64.5	58.0	8.5	72.0	59.5	63.0	61.0
Order of the above	7	4	2	6	7	1	5	3	4
Content of iron (Fe) %	1.600	1.527	1.955	1.355	2.163	1.990	1.280	0.966	1.191
Order of the above	3	4	3	4	1	2	5	7	6
Content of manganese (MnO) %	0.0376	0.0407	0.0055	0.0375	0.0030	0.0403	0.0400	0.0325	0.0408
Order of the above	2	1	6	5	7	2	3	4	1

6) Effect of reaction upon soil-catalysis.

The acceleratory and inhibitory effects of alkali and acid added to sample on its catalytic action were observed in all experiments of the preceeding chapters where such addition was made.

The present writer also found by experiment that if calcium oxide is added to soil, the limed soil decomposes all of hydrogen peroxide when it is shaken with 1% hydrogen peroxide in spite of the fact that the soil-particles have been completely coagulated.

The cause of the above acceleration and inhibition might be due to the peptizing and coagulating effect of alkali and acid, but there is no reason to neglect the effect of reaction itself.

It is a well known fact that hydrogen peroxide decomposes itself in presence of alkali and this does not happen in presence of acid, but it is very important for this case to determine the degree of the effect of alkali and acid on this decomposition.

For this purpose, the following experiments were conducted.

Exp. 1. The writer added 25 c.c. of 0.8% hydrogen peroxide to 25 c.c. of hydrochloric acid and sodium hydroxide solution in various concentrations as in the next table, shaken one hour, and the quantity of hydrogen peroxide decomposed was determined as shown in the following table.

Concentration		H_2O	$\frac{1}{5000}N$	$\frac{1}{1000}N$	$\frac{1}{500}N$	$\frac{1}{200}N$	$\frac{1}{100}N$	$\frac{1}{50}N$	$\frac{1}{25}N$
HCl	Undecomposed[1]	10.00	10.00	10.05	10.15	10.05	10.00	10.00	10.10
	Decomposed[2]	0	0	−0.50	−1.50	−0.50	0	0	−1.00
NaOH	Undecomposed[1]	10.00	10.00	10.00	9.75	9.55	9.40	9.05	9.05
	Decomposed[2]	0	0	0	2.50	4.50	6.00	9.50	9.50

The above result shows that the presence of hydrochloric acid inhibits the decomposition of hydrogen peroxide by shaking and that of sodium hydroxide accelerates it.

But these acceleration and inhibition are not remarkable and are scarcely to be observed in the dilution lower than 1/1000 — 1/50[3] normal.

Exp. 2. To 25 c.c. of sodium hydroxide and hydrochloric acid in the same different concentrations as above, was added 1 gr. of carbon powder (carbo depuratus), shaken and determined the quantity of hydrogen peroxide decomposed, as in the next table, after being treated the whole with peroxide solution in exactly the same manner as in Exp. 1.

Concentrations		H_2O	$\frac{1}{5000}N$	$\frac{1}{1000}N$	$\frac{1}{500}N$	$\frac{1}{200}N$	$\frac{1}{100}N$	$\frac{1}{50}N$	$\frac{1}{25}N$
HCl	Undecomposed[3]	7.68	7.78	8.38	8.88	9.30	9 35	9.30	9.40
	Decomposed[4]	23.20	22.20	16.20	11.20	7.00	6.50	7.00	6.00
HONa	Undecomposed[4]	7.68	7.35	6.35	4.53	2.23	0.60	0.15	0
	Decomposed[5]	23.20	26.50	36.50	54.70	77.70	94.00	98.50	100.00

0.4% H_2O_2 shaken one hour—undecomposed[1] 10.00

From the above table, we see also the acceleration and inhibition of the decomposition by charcoal of hydrogen peroxide by alkali and acid, and that the degree of the effect of alkali and acid is markedly greater in the presence of carbon powder.

These effects are clearly observed in the dilution of 1/10000 normal in this experiment instead of 1/1000 — 1/50 normal in Exp. 1.

The above remarkable increase in effect of alkali and acid, owing to the precence of carbon particles may partly be due to the peptization and coagulation of particles by alkali and acid, but the result of the next experiment clearly indicates that it must also be attributed to the effect of reaction itself.

1) For 5 c.c. of the solution.
2) For 50 c.c. of the solution.
3) 1/1000 normal in case of alkali and 1/50 normal in case of acid.
4) For 5 c.c. of the filtrate.
5) For 50 c.c. of the filtrate.

Exp. 3. With 1 gr. of quartz-sand, the same experiment as conducted in Exp. 2. was carried out and the result is given in the following table.

			NaOH				HCl			
		O	$\frac{1}{10}$N	$\frac{1}{25}$N	$\frac{1}{50}$N	$\frac{1}{100}$N	$\frac{1}{10}$N	$\frac{1}{25}$N	$\frac{1}{50}$N	$\frac{1}{100}$N
With quartz-sand	Undecomposed[1]	5.05	0.00 all decomposed	2.70	3.18	3.90	5.10	5.10	5.10	5.10
	Decomposed[2]	0.00	decomposed	23.50	18.70	11.50	−0.50	−0.50	−0.50	−0.50
Without quartz-sand	Undecomposed[1]	5.05	2.58	3.85	4.45	4.65	5.05	5.05	5.05	5.05
	Decomposed[2]	0.00	24.70	12.00	6.00	4 00	0.00	0.00	0.00	0.00

The above result, as in case of carbon powder, shows also the remarkable effect of alkali and acid in acceleration and inhibition of the decomposition of hydrogen peroxide.

Since silicic oxide both in forms of gel and sol, can not decompose hydrogen peroxide as has been already shown by experiment, the above acceleration and inhibition can not be attributed to the peptization and coagulation of quartz-sand particles and they must due to reaction itself.

From the results of Exp. 1—3, it is to be concluded that the acceleration and inhibition of catalysis by the addition of alkali and acid, is not only due to physical change in the soil-particles but also to the change in soil-reaction itself; and the marked increase of soil-catalysis after liming must be attributed to the alkaline reaction of soil produced.

In order to determine the existence of correlation between reaction[3] and catalytic power[4] of soil, the present writer measured both in the usual way and obtained the following result. This shows no definite relation.

Soil No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Hydrogen peroxide decomposed	47.0	89.3	67.0	75.8	43.3	28.0	62.8	83.8	48.0	67.8	64.5	58.0	8.5	72.0	59.5	63.0	61.0
Order of the above	8	1	5	5	9	10	6	2	7	4	2	6	7	1	5	3	4
PH	7.05	7.09	7.09	7.18	6.89	7.03	7.18	6.99	6.93	6.89	6.75	6.75	7.09	7.35	6.66	7.09	6.97
Order of the above	5	3	4	1	10	6	2	7	8	9	5	6	3	1	7	2	4

1) For 5 c.c. of the filtrate.

2) For 50 c.c. of the filtrate.

3) Reaction is expressed in terms of hydrogen ion concentration obtained by hydrogen electrode methode in the extract of 10 gr. soil with 100 c.c. of distilled water.

4) The method of determination of the catalytic power has already been recorded in case of humus.

Since there are many factors which influence soil-catalysis, there is no reason to conclude from the above table that soil-reaction has no effect upon the decomposition of hydrogen peroxide by soil, but rather it is reasonable to suppose more definite results would be obtained if we used samples whose reactions differ more.

3. Bacterial and enzymic actions on soil-catalysis.

The effect of bacteria and enzyme on soil-catalysis has been investigated by J. König, J. Hasenbäumer and E. Coppenrath,[1] D. W. Way and P. L. Gile[2] and O. Schreiner and M. X. Sullivan.[3]

But the method determing these effects used by these investigators is not entirely objectionable.

They assumed the decrease of activity of the sample after its being exposed to heat, to carbon bisulphide, chloroform, prussic acid, hydrogen sulphide, iodine and mercuric chloride etc.

Not only does the exposure of sample to the above mentioned reagents limit the action of the bacteria and enzyme in sample, but also it may, sometimes at least, cause the change in the physical condition of particles.

From this circumstances, the above decrease may result not only from the destruction of bacteria and enzyme, but also from the change in the physical state of the particles.

But, if the result of the treatments as above mentioned, is always the same in all samples from various sources, it may be safely concluded that the decrease is due to bacteria and enzyme.

With this consideration, the writer made on experiment on the effect of bacteria and enzyme to soil-catalysis.

The treatments in the experiment are as follows;

1) 10 grs. soil received the addition of 25 c.c. of H_2O, shaken for 3 hours.

2) 10 grs. soil received the addition of 25 c.c. of H_2O and 10 c.c. of Toluol, shaken for 3 hours.

3) 10 grs. soil heated in Koch's sterilizer for 3 hours.

4) 10 grs. soil received the addition of 25 c.c. of 0.2% mercuric chloride, shaken for 3 hours.

After the above treatment, to each was added 25 c.c. of 0.2 or 0.4%[4]

1) König, J., Hasenbäumer, J. and Coppenrath, E., Landw. vers. stat. 63 (1906) s. 471.

2) Way, D. W. and Gile; P. L., Porto Rico. stat. circ. 9, p. 3—13, abs. E. S. R. 21 (1909) p. 220.

3) Schreiner, O. and Sullivan, M. X., Science n. ser. 33 (1911) No. 844, p. 399, abs. E. S. R. 25 (1911) p. 320.

4) No. 1 to 10, with 0.25% and No. 11 to 17, with 0.2% H_2O_2.

S. OSUGI:

Soil No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Hydrogen peroxide decomposed.																	
Control (H₂O)	47.0	89.3	67.0	75.8	43.3	28.0	62.8	83.8	48.0	67.8	64.5	58.0	8.5	72.0	59.5	63.0	61.0
Toluol	48.8	88.0	65.5	70.8	40.8	24.8	61.0	85.0	51.3	66.0	65.0	58.0	10.0	59.5	59.5	62.7	60.5
HgCl₂	24.3	31.8	29.3	63.3	21.8	13.6	20.8	70.8	29.8	37.8	47.5	30.5	5.5	47.5	32.5	42.5	32.0
Heated	27.8	31.8	27.3	66.8	18.8	10.6	25.3	64.3	29.3	32.8	50.5	44.5	5.5	58.5	31.0	45.0	40.5
Percentage composition of the quantity of the peroxide decomposed.																	
Control (H₂O)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Tolnol	103.90	98.56	71.40	93.46	94.25	88.54	96.99	101.15	108.70	97.02	100.75	100.00	118.00	82.71	100.00	99.69	96.19
H₂O-Toluol[1]	-39	1.44	28.60	6.54	5.75	11.46	3.01	-1.15	-6.70	2.98	-0.75	0.00	-18.00	17.29	0.00	0.31	3.81
HgCl₂	51.76	35.62	31.94	83.56	50.36	48.55	33 07	84.25	61.98	55.57	73.63	52.46	64.90	66.03	54.60	67.58	50.88
Toluol-HgCl₂[2]	52.14	62.94	39.49	9.90	43.89	40.00	63.92	16.90	44.72	41.45	27.12	47.54	53.10	16.68	45.40	32.11	45.31
Heated	61.34	35.62	29.76	88.18	43.43	37.84	40.23	76.50	60.90	48.22	78.28	76.54	64.90	81.32	52.08	71.55	64 40
Toluol-heated[3]	42.56	72.94	41.64	4.35	50.82	50.70	56.76	24.65	45.80	48.80	22.47	23.46	53.10	1.39	47.92	28.14	31.79

1) Action of enzyme or enzyme like substances.

2) and 3) Action of bacteria.

hydrogen peroxide, shaken for one hour and was determined the quantity of the decomposed hydrogen peroxide and calcutation was made on the difference of catalytic power of

1) Soil untreated and soil treated with Toluol.
2) Soil treated with Toluol and soil heated.
3) Soil treated with Toluol and soil treated with mercuric chloride.

From the above result, we see that bacterial effect on soil-catalysis is rather small and it may not exceed 10% of the activity of original soil, but the effect of enzyme or enzyme like substances is quite remarkable and it may be between 30—50% of the activity of original soil and the remaining activity may due to inorganic and organic soil-constituents.

Among these constituents, manganese oxide plays the most important part, ferrie oxide comes next; and humus, the least.

Soil-reaction also may have effect on the decomposition of hydrogen peroxide, especially when it is distinct.

Summary.

The results obtained in the present investigation are summarized as follows;

1) Soil decomposes hydrogen peroxide to varying degrees.
2) Coagulation and peptization of soil-particles result in the change in the magnitude of soil-catalysis.

   Usually, any peptizing action makes the power greater and coagulating action effects it in the reverse way.
3) Silicic acid and silicates, aluminium oxide and silicate have no action on hydrogen peroxide and accordingly, these constituents in soil may not be the cause of soil-catalysis.
4) Humus, ferric oxide (and ferric compounds) and manganese oxide (and manganese compounds) both in forms of sol and gel, show very marked catalytic power and these substances may be main constituents giving soil so distinct activity on hydrogen peroxide, although the writer could not obtain any quantitative relation between soil activity and soil-content of these constituents.

   Among the three above enumerated, the action of manganese is largest and that of humus, the least.

   The peptizing and coagulating agents upon the catalytic action of these substances, cause almost the same change as experienced in case of soil with a few exceptional cases.
5) Sulphate and chloride of manganese and iron in the concentration of 0.0063—0.025%, show no power to decompose hydrogen peroxide.
6) Alkali and acid reaction in soil may effect soil-catalysis, at least, in two ways.

   They introduce change in the physical state of soil-particles, which results in the change in soil-catalysis and also they may play important part in soil-catalysis by reaction itself, (alkali-reaction promotes catalysis and acid-reaction acts in the reverse way) especially when soil reacts distinctly.

7) Bacterial effect on soil-catalysis, seems to be small; and that of enzyme like substances seems to be considerable; and inorganic and organic soil-constituents mentioned in 4, play the greatest part in soil-catalysis.

Acknowledgements.