MATHEMATICAL STUDIES ON THE INFLUENCE OF TEMPERATURE AND MOISTURE ON NITRIFICATION

BY

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Introduction

It is a well known fact that nitrification is the phenomena of transforming ammoniacal nitrogen into nitric nitrogen by the action of microorganisms. The nature of this biochemical process was proved, some years ago, by one[1] of the authors, to be autocatalitic monomolecular reaction.

The influences of enviromental conditions upon the nitrification have been studied hitherto by many investigators,[2] from the stand point of soil bacteriology. But no papers have as yet been presented which formulate the relation between the sorrounding conditions and the bacterial activity. On this account, we here attempt to elucidate a phase of the formulation.

The present paper contains the results obtained in experiments with temerature and moisture.

Materials used for Experiment

The soil used was taken from the unmanured plot in the experimental field of our University, in which indian corn had been cultivated continuously for five years without manures.

For the experiment air dried soil was used after it was passed through a 0.5 mm. sieve.

The moisture content and water capacity of the soil was determined to be 7.9 % and 53.7 % respectiuely.

Ammoniunm sulfate was used as the material to be nitrified, 0.0472 g. of which being equivalent to 10 milligrams of nitrogen.

[Transact. Sapporo Nat. Hist. Soc., Vol. XII, Pt. 2, 1932]

Experiment on the Influence of Temperature

Ten grams of the soil were mixed with ammonium salfate equivalent to 10 milligrams of nitrogen. To this was added water, equivalent to 70% of the water capacity of the soil. After mixing well, the soil was placed in a 150 c. c. Erlenmayer flask with a stoppered cork. The flask was then allowed to stand in a thermostat at constant temperature of 0°C, 12°C, 20°C, 27°C, 32°C and 37°C respectively.

After the definite intervals of time indicated in Table 1, the flask was taken out from the thermostat and the nitrates formed were determined colorimetrically by the method of phenyldisulfonic acid as follows:

From 100 c. c. to 300 c. c. of distilled water were added to the flask according to the amount of nitrate formed. After addition of a small amount of aluminium-hydroxide, it was shaken for a few minutes in order to obtain a clear liquid. After standing for an hour it was filtered through dried filter paper. The definite amount of the filtrate thus obtained was placed in a glass basin and evaporated nearly to dryness on a water bath. 1 c. c. of phenyldisulfonic acid was then added to the residue and mixed. After standing for 15 minutes, about 15 c. c. of distilled water were added and well stirred. Ammoniumhydroxide was then added until the solution was alkaline, then distilled water bringing it up to 500 c. c.. The yellow color produced was compared colorimetrically with the standard solution which contains 0.01631 g. of pure crystallized potassium nitrate to a litre.

The results obtained are tabulated as follows.

Table 1 Amount of Nitrate produced in milligrams

Time (days)	0°C	12°C	20°C	27°C	32°C	37°C
0	0.065	0.065	0.065	0.065	0.065	0.065
1	0·065	0.065	0.065	0.065	0.065	0.065
2	0.065	0.070	0.080	0.083	0.092	0.085
3	0.066	0.077	0.105	0.107	0.114	0.110
4	0.068	0.096	0.116	0.126	0.150	0.134
5	0.c80	0.115	0.122	0.160	0.214	0.186
7	0.081	0.120	0.135	0.180	0.330	0.192
9	0.080	0.140	0.154	0.272	0.410	0.268

Time (days)	0°C	12°C	20°C	27°C	32°C	37°C
11	0.085	0.158	0.263	0.395	0.614	0.384
13	0.109	0.173	0.412	0.507	0.769	0.507
15	0.105	0.175	0.522	0.660	0.883	0.550
18	0.105	0.190	0.665	0.805	0.979	0.603
21	0.109	0.190	0.771	0.904	1.054	0.650
24	0.107	0.210	0.861	0.983	1.085	0.685
27	0.099	0.214	0.902	1.021	1.106	0.720

As seen in the above table, the bacterial activity at a temperature of 0°C is very feeble. It is then difficult to prove whether the nitrification at this temperature proceeded autocatalitically or not. At the temperature of 12°C, it was barely seen to be autocatalytic. At a temperature higher than 12°C, it proceeded typically according to the monomolecular reaction of autocatalytic.

The equation of autocatalytic monomolecular reaction is

$$\log \frac{X}{A-X} = K(t-t_1)$$

where X: Amount of nitrate produced at the intervals of time t
A: Maximum amount of nitrate produced
t_1: Time for ½A nitrate production
K: Constant

In the above equation the constants are K, A and t_1. To see the influence of temperature on the process, it is then reasonable to compare the value of the constants. Among these, however, the comparison of constant K alone is seen to be most reasonable, as the value of K represents the velocity of the reaction.[3]

So the authors attempted to deduce a formula which shows a change of the value of K in relation to temperature.

In Table 2 the value of K is calculate from the data in Table 1;

Table 2 Values of K calculated from Data in Table 1

Temperature (T)	K
12 C	0.069±0.005
20 C	0.091±0.002
27 C	0.106±0.001
32 C	0.120±0.001
37 C	0.105±0.003

In order to find the influence of temperature upon the constant K, the authers calculated, at first, the value of the so-called Q_{10} quotient[4] as follows:

$$Q_{10}=\left(\frac{K_{20}}{K_{12}}\right)^{\frac{10}{20-12}}=\left(\frac{0.091}{0.061}\right)^{\frac{5}{4}}\doteqdot 1.6$$

$$Q_{10}=\left(\frac{K_{27}}{K_{20}}\right)^{\frac{10}{27-20}}=\left(\frac{0.106}{0.091}\right)^{\frac{10}{7}}\doteqdot 1.3$$

$$Q_{10}=\left(\frac{K_{32}}{K_{27}}\right)^{\frac{10}{32-27}}=\left(\frac{0.120}{0.106}\right)^{5}\doteqdot 1.3$$

$$Q_{10}=\left(\frac{K_{27}}{K_{32}}\right)^{\frac{10}{32-27}}=\left(\frac{0.105}{0.120}\right)^{5}\doteqdot 0.7$$

As the results show, the value of K increases 1.3 times with each increas of 10°C in temperature until it reaches 32°C, then it decreases to 0.7 times as seen at 37°C.

These results tell us that the nitrification process shows the tendency of pure chemical reaction at the temperatures between 12 and 32°C. But a rapid decrease of the value of Q_{10} in temperature above 32°C, clearly shows that the process is biochemical.

Then to represent mathematically the influence of temperature we must take into a consideration especially these relationships existing between the temperature and the nature of the phenomena. So the writers deduced the following empirical equation with the aid of the method of least squares paying attention to the above facts.

$$K=0.038+0.014\frac{T}{5}-0.015\,e^{\frac{T-32}{5}}$$

The values of K calculated form the above equation are compared with the values of K cited already in Table 2 as follows:

Table 3 The Values of K calculated from above Equation and in Table 2

Temperature	K in Table 2	K calculated	difference
12 C	0.069	0.074	0.005
20 C	0.c91	0.074	0.006
27 C	0.106	0.108	0 002
32 C	0.120	0.113	0.007
37 C	0.105	0.106	0.001

The above table shows that both the values K agree well.

Experiment on the Influence of Moisture

On the effect of moisture content in soils on nitrification, the results obtained are shown in Table 4.

The experiment was carried out in the constant temperature of 30°C having the moisture content of soils at 20%, 40%, 50%, 60%, 70% and 80% of the water bapacity.

Table 4 Amount of nitrate produced in milligrams

Time (days)	20%	40%	50%	60%	70%	80%
0	0.065	0.065	0.065	0.065	0.065	0.065
1	0.065	0.065	0.065	0.065	0.065	0.065
2	0.c65	0.067	0.071	0.090	0.092	0.092
3	0.088	0.083	0.087	0.110	0.125	0.098
4	0.114	0.149	0.140	0.140	0.143	0.140
5	0.115	0.160	0.180	0.182	0.210	0.180
7	0.150	0.224	0.235	0.250	0.295	0.252
9	0.151	0.240	0.340	0.363	0.410	0.371
11	0.152	0.260	0.401	0.494	0.600	0.501
13	0.145	0.281	0.535	0.642	0.786	0.678
15	0.152	0.297	0.643	0.722	0.850	0.770

Time (days)	20%	40%	50%	60%	70%	80%
18	0.145	0.308	0.739	0.846	0.924	0.880
21	0.152	0.320	0.800	0.905	1.003	0.952
25	0.152	0.340	0.875	0.993	1.090	1.002
30	0.140	0.340	0.897	1.028	1.100	1.002

The values of K were first calculated from the above data putting them into the autocatalytic monomolecular equation and secondly, the Q_{10} quotient was calculated from the value of K as shown in Table 5.

Table 5 The Values of K and Q_{10}

% of water capacity (M)	K	Q_{10}
40	0.090 ± 0.005	
50	0.102 ± 0.002	1.1
60	0.110 ± 0.001	1.1
70	0.119 ± 0.003	1.1
80	0.114 ± 0.000	0.9

In the case of the influence of moisture content, the change of K can be represented by linear function up to 70 % of the water capacity, but abobe 70% it decreases gradually.

So the writers deduced the following empirical equation as in the case of temperature effect.

$$K = 0.056 + 0.0018\frac{M}{5} + 0.005\ e^{-\frac{M-70}{5}}$$

And the values of K calculated from the above equation are compared with the values of K cited already in Table 5 as follows:

Table 6 Values of K calculated from the above Equation and in Table 5

% of water capacity	K in Table 5	K calculated	Difference
40	0.090	0.092	0.002
50	0.102	0.101	0.001
60	0.110	0.110	0.000
70	0.119	0.116	0.003
80	0.114	0.114	0.000

Summary

1) The influence of enviromental conditions on the nitrification process were studied mathematically. In the present experiment, temperature and moisture were taken as the enviromental conditions.

2) Considering that the influence of the enviromental conditions on the nitrification process can be represented by the change of reaction constant K of the autocatalytic monomolecular equation which represents the process mathematically, the writers observed the influence of the change of temperature and moisture on the value of K.

3) Within the extent of temperature and moisture at which the reaction can proceed autocatalytically, the value of K increases linearly as the temperature and the moisture increase, but after it reaches a certain point of increment the value of K decreases rapidly.

So the change of K can be represented empiriclly by an equation as follows:

In the case of the effect of temperature,

$$K=0.038+0.014\frac{T}{5}-0.015\ e^{\frac{T-32}{5}}$$

In the case of the effect of moisture content,

$$K=0.056+0.0018\frac{M}{5}-0.005\ e^{\frac{M-70}{5}}$$

Literature

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摘　　要

硝酸化生作用に及ぼす溫度及濕度の影響に關する數學的硏究

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(1) 硝酸化生作用に及ぼす溫度及び濕度の外圍條件につき、之れが影響を數學的に考察した。

(2) 而して、此の種外圍條件の影響は硝酸化生作用を示す所の自己觸媒的一分子反應式の恒數Kの變化に依つて表はさるるものとしてKの上に及ぼす是等條件の影響を測定した。

(3) 反應の自己觸媒的一分子反應的に營まれ得る條件を得るときは、其の條件の好都合なるに從がひKの値は直線的に增加し、一定限度に到つて急激に減少する傾向を示す。

溫度の影響の場合には

$$K = 0.048 + 0.014\frac{T}{5} - 0.015\ e^{\frac{T-32}{5}}$$

濕度の影響の場合に於ては

$$K = 0.056 + 0.0018\frac{T}{5} - 0.005\ e^{\frac{M-70}{5}}$$

なる實驗式にて示し得ることを認めた。