

Effect of Zeolite on the Decomposition Resistance of Organic Matter in Tropical Soils under Global Warming

Mai Thanh Truc, Masao Yoshida

Abstract—Global temperature had increased by about 0.5°C over the past century, increasing temperature leads to a loss or a decrease of soil organic matter (SOM). Whereas soil organic matter in many tropical soils is less stable than that of temperate soils, and it will be easily affected by climate change. Therefore, conservation of soil organic matter is urgent issue nowadays. This paper presents the effect of different doses (5%, 15%) of Ca-type zeolite in conjunction with organic manure, applied to soil samples from Philippines, Paraguay and Japan, on the decomposition resistance of soil organic matter under high temperature. Results showed that a remain or slightly increase the C/N ratio of soil. There are an increase in percent of humic acid (PQ) that extracted with $\text{Na}_4\text{P}_2\text{O}_7$. A decrease of percent of free humus (fH) after incubation was determined. A larger the relative color intensity (RF) value and a lower the color coefficient ($\Delta\log K$) value following increasing zeolite rates leading to a higher degrees of humification. The increase in the aromatic condensation of humic acid (HA) after incubation, as indicates by the decrease of H/C and O/C ratios of HA. This finding indicates that the use of zeolite could be beneficial with respect to SOM conservation under global warming condition.

Keywords—Global warming, Humic substances, Soil organic matter, Zeolite.

I. INTRODUCTION

THE average facade temperature of the globe has augmented more than one degree Fahrenheit since 1900 and the speed of warming has been almost three folds the century long average since 1970 (IPCC, 2007). There is a general expectation that increasing temperature leads to increase in both net primary productivity which provides the input to soil organic C, and the rate of soil organic matter decomposition which determines the loss of soil organic C. Increased temperature may lead to more rapid breakdown of soil organic matter and even small increases in temperature may prompt large releases of C from soils (Richard T. Conant *et al*, 2008) [8]. Schimel *et al.*, 1994 summarize modeling and data-based predictions of C release (11.1 to 33.8 Pg C) from SOM for a 1°C increase in global mean annual temperature [10]. Hence, it seems likely that soil organic C will decrease with increasing temperature due to climate change. In addition, organic matter

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decomposition rates in tropical soils are generally faster than in temperate soils because decay of nonlabile fraction is generally faster (Sheila M. Ross, 1993) [9]. Thus, the effects of climate change on the rate of soil organic matter decomposition in high latitudes are expected to be much larger.

SOM plays essential role, without SOM, the Earth's surface would be a sterile mixture of weathering minerals. Focusing on understanding the significance and learning how to enhance the quality and quantity of SOM may lead to sustainable agriculture. Besides increasing soil organic matter, the ways to reduce its decomposition rate needs to be understood. One of the measures considered highly effective, biologically justified and environmentally safe, especially on degraded and other soils having unfavourable productive traits for crop cultivation, is the use of natural zeolite mineral (Polat *et al.*, 2004; Beqiraj *et al.*, 2008) [7].

Zeolite's component are SiO_2 , Al_2O_3 and Fe_2O_3 . One measure of this property is the cation exchange capacity (CEC). The application of zeolite to soils increases their E.C and as a result, it increases nutrient retention capacity. Futhermore, the adition of zeolite usually increase pH levels (Ming.DW and Boettinger) [6]. Hence, zeolite acts as a slow release fertilizer, giving the plant access to water and nutrients for longer, which results in a significant saving in water resources and reducing the amount of fertilizer to be applied. Natural zeolites are characterized by negatively charged frameworks, with a high cation exchange capacity and specific cation selectivity (Colella, 1996), it is important to regonize that interactions of zeolitic tuffs with humic substances depend on the features of the bridge cation [2]. Thus, the hypothesis is given a complexation between oxy of zeolite components and organic acid that take form organo-metallic when zeolite is applied to the soil. And, whether organo-metallic is a decomposition resistance of soil organic matter, hence the research was performed in order to investigate the effect of its on the decomposition resistance of organic matter in tropical soils under global warming condition.

II. EXPERIMENTAL METHODS

The experiment was carried out with soil samples from Philippines (Ph), Paraguay (Pa) and Japan (J). The chemical characteristics of the soil are shown in Table 1. Ca-zeolite was used for the study and relevant properties are shown in Table 2. Different doses (5%, 15%) of Ca-zeolite type in conjunction with 25% organic manure (OM) was applied to soil samples. The experiment was consisted of 18 treatments. Sample codes for treatments as follow: S1, S2, S3, SO1, SO2, SO3 (S: soil;

O: organic manure; 1, 2, 3 : 0, 5, 15% zeolite, respectively). The incubation was carried out in a soil flask for a durations of 1, 3 and 6 months all with a temperature of 40°C and relative humidity of 65 to 70%. During the incubation period, soil treatments were irrigated every three days depending on the vapo-transpiration value which was measured gravimetrically. Soil samples were collected after 1, 3, and 6 months, air dried, crushed and pass through a 0.5-mm mesh sieve and then used in the laboratory analyses.

TABLE I
SOIL AND ORGANIC MANURE CHEMICAL PROPERTIES PRIOR TO EXPERIMENT

Property	Philippines soil (Ph)	Paraguay soil (Pa)	Japan soil (J)	Organic manure (O)
Total C (%)	2.44	2.06	5.82	5.64
Total N (%)	0.15	0.17	0.38	1.62
C/N	16.30	12.10	15.30	3.50
Na (me/100 g soil)	110.86	15.95	3.26	550.81
K (me/100 g soil)	119.22	22.52	32.40	1436.46
Ca (me/100 g soil)	1584.10	141.49	33.74	990.76
Mg (me/100 g soil)	264.56	11.34	12.50	658.00
CEC (Cmol _c /kg)	30.18	20.66	20.88	61.19

TABLE II
CHEMICAL CHARACTERISTICS OF CA-ZEOLITE TYPE

Property	Value	Ca-Zeolite type
CEC	cmol (+)/kg	257.9
pH _{H2O}		10.0
Na	cmol (+)/kg	109.4
K	cmol (+)/kg	16.5
Ca	cmol (+)/kg	309.8
SiO ₂	%	46.5
Al ₂ O ₃	%	24.0
CaO	%	12.0

Source: Based on Maeda corporation (2005)

The procedure determine humus composition was used the method of successive extraction with NaOH followed by Na₄P₂O₇ reported by Kumada *et al.* (1967). The humic acid were classified on the basis of their absorption spectrum and the parameters of humification ($\Delta\log K$ and RF value), these variables can be simply converted to the variables used in this study as follows: $\Delta\log K = \log K_{400} - \log K_{600}$, where K₄₀₀ and K₆₀₀ are the absorbances at 400 and 600 nm in 0.1 N NaOH, respectively; $RF = K_{600} \times 1,000/c$, where c is the amount of 0.1 N KMnO₄ consumed by the 30 ml of humic acid solution used for the absorption spectrum measurement (Kumada *et al.*, 1967). The percentage of humic acid in extracted humus ($PQ = HA/(HA+FA) \times 100$) was calculated, FA is fulvic acid (Yoshida *et al.*, 1978) [11].

Carbon, hydrogen and nitrogen were determined from the dried powder humic acid samples and soil samples with a Yanaco CHN CORDER MT-6 to measure degree of unsaturation ($DUS = (2[C] + 2 - [H] + [N]) / 2[C] \times 100$) (Yoshida *et al.* 1982; Timofeevna *et al.*, 2006).

III. RESULTS AND DISCUSSION

A. Effect of Zeolite application on Carbon to nitrogen (C/N) ratios

The changes in the C/N ratios of soil reflect the rate of decomposition of organic matter and this results in the release (mineralisation) or immobilization of soil nitrogen. A decrease in the C/N ratio from 0 month to 6 months for the untreated soil samples at significant levels. That is a result of decomposition of soil organic matter quickly during incubation time under high temperature. Because the organic molecules in organic matter were broken down into simpler organic molecules. Meanwhile, there was a general higher in the C/N ratio with 5 and 15% zeolite application compared with untreated soil samples after 6 months incubation (Fig.1). The treatment applied 15% zeolite gave the highest of C/N ratios at 18.2 (Ph3) and 10.8 (PhO3); 16.4 (J3) and 9.1 (JO3); and 15.0 (Pa3). It means that nitrogen contents were much mineralized during decomposition process, while there was a gradual carbon condensation for the soil by the combination of zeolite and organic matter become stronger than before that made the decomposition of soil organic matter slow down.

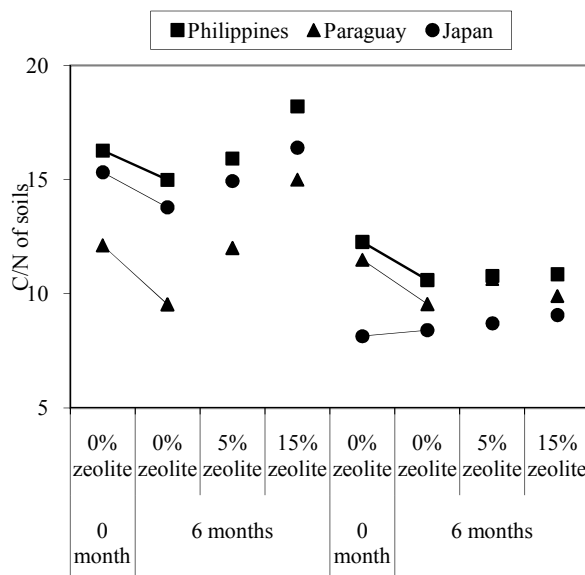


Fig. 1 Changes in C/N ratio of soils studying after 6 months incubation

B. Effect of Zeolite application on soil humic substances

In Fig. 2 can be observed that the treatments applied zeolite combine with organic manure of all soils studying gave a higher carbon contents of HA than the treatments applied only zeolite. The carbon contents of HA from 5 to 15% zeolite application were all higher than that of HA from untreated soil samples after 6 months of incubation. Addition of 5% and 15% zeolite to soils significantly increased "combined" form of HA (HA extracted by Na₄P₂O₇), conversely, "free" form of HA (HA extracted by NaOH) was decreased. According to Kumada and Ohta (1965), humus extracted with NaOH

presents a very weakly combined form with polyvalent cations or free form, whereas the humus extracted with $\text{Na}_4\text{P}_2\text{O}_7$ presents a strongly combined form with polyvalent cations and clay minerals [5]. In addition, the humus extracted with $\text{Na}_4\text{P}_2\text{O}_7$ is supposed to be more stable than that extracted with NaOH (Kumada *et al.*, 1981). Therefore, an increase “combined” form of HA in humus fractions means the formation of organic-metal-mineral complexes is more stable in soils that make the decomposition of humic substances will slower.

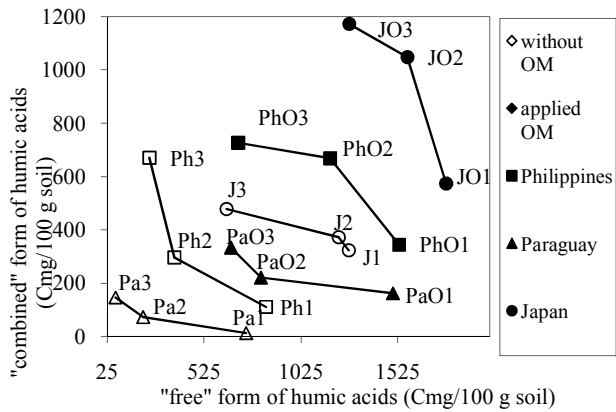


Fig. 2 Relationship of “combined” form of humic acid and “free” form of humic acid in soils studying after 6 months of incubation

Addition of zeolite to soils significantly increased PQ_2 (the percent of HA value of “combined” form of HA extracted by $\text{Na}_4\text{P}_2\text{O}_7$), conversely, PQ_1 (the percent of HA value of “free” form of HA extracted by NaOH) was decreased following raising zeolite rates after 6 months incubation (Fig. 3).

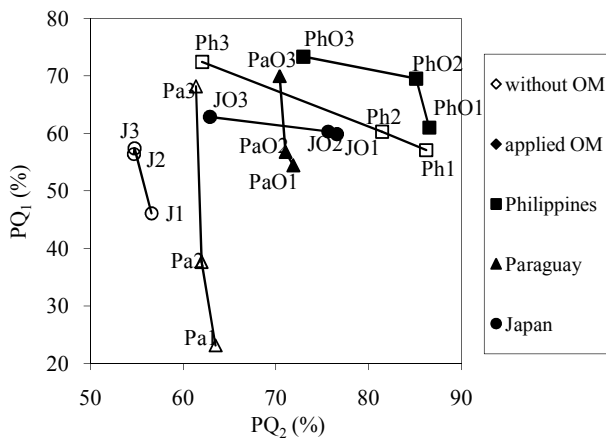


Fig. 3 Relationship of percent of humic acid in extracted humus by NaOH (PQ_1) and $\text{Na}_4\text{P}_2\text{O}_7$ (PQ_2) in soils studying after 6 months incubation

This results suggested that the relative proportion of HA increased while FA decreased with increasing dose of zeolite. As we know humic acid, which is the most resistant fraction to

microbial degradation of the organic matter in soil, are complex polymeric HA with a wide range of molecular weights. Therefore, an increase amount of HA contents in humus fraction will resist the decomposition of humic substance by stable organic clay with zeolite complexes.

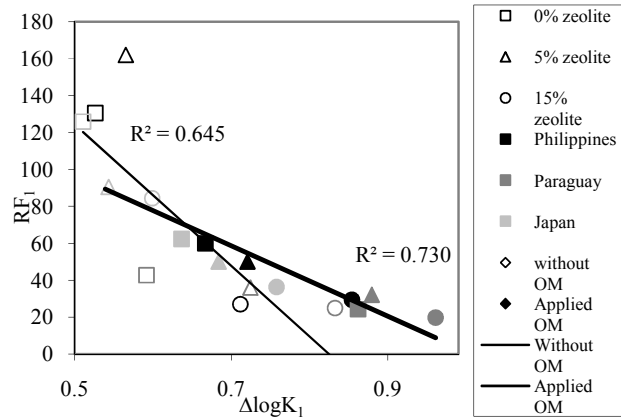


Fig. 4 Relationship of RF_1 and $\Delta\log K_1$ with zeolite rates in soil studying after 6 months incubation (HA extracted by NaOH)

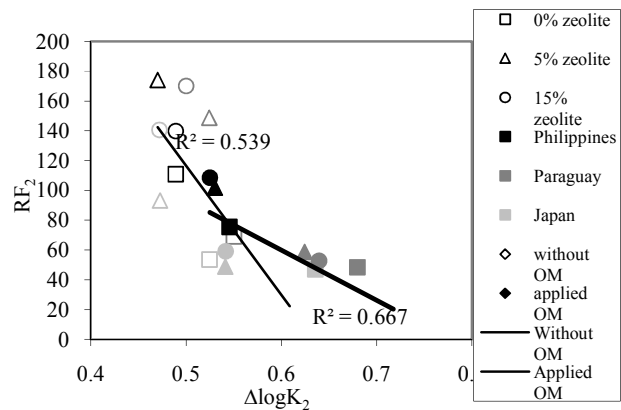


Fig. 5 Relationship of RF_2 and $\Delta\log K_2$ with zeolite rates in soil studying after 6 months incubation (HA extracted by $\text{Na}_4\text{P}_2\text{O}_7$)

The $\Delta\log K$ and RF have been used as indexes for the degree of humification of HA (Kumada, 1987) [4]. As for alkali-extractable humic acids, when zeolite rates were increased from 0 to 15%, the $\Delta\log K_1$ of HA increased, whereas, RF_1 of HA decreased in both of groups without and applied organic manure with a correlative at $r^2 = 0.65$ and $r^2 = 0.73$, respectively (Fig.4). This indicates the HA formed during humification process of soil organic matter has a lower humification degree in 5 and 15% zeolite application to soils. However, the reverse was observed as to pyrophosphate-extractable humic acids, the decrease of $\Delta\log K_2$ and the increase of RF_2 compared with those of control soils with a correlative at $r^2 = 0.54$ and $r^2 = 0.67$, respectively (Fig.5). The highest percent of humic acid in “combined” form of HA (PQ_2) was obtained in treatments applied 15% zeolite wherein the lowest mean average values of $\Delta\log K_2$ was also obtained

in this study. According to the results, humus composition may be concluded that part of the free humus, particularly the humic acids which have a higher degree of humification were transformed into calcium-combines forms, and that the extent of the transformation decreased in soils (Ryosuke Shiroya and Kyoichi Kumada, 1976). Therefore, when $\Delta \log K$ decrease and RF increase, soil organic matter has a higher humification degree that means organic matter will decompose slowly.

According to Baranciková *et al.* (1997) the diagram of H/C atomic ratio versus O/C atomic ratio may be considered as a graphical-statistical representation which indicates the changes in properties occurring during coalification reactions such as oxidation, dehydrogenation, dehydration, demethanation and decarboxylation [1]. At treatments applied zeolite in soils studying, the diagram of atomic O/C versus H/C with incubation time (Fig.6) shows a general tendency that a decrease in O/C and H/C of HA extracted by NaOH and $\text{Na}_4\text{P}_2\text{O}_7$ are observed in both of groups without and applied organic manure with a correlative at $r^2 = 0.63$ and $r^2 = 0.62$, respectively, whereas treatments without zeolite were in the opposite direction from 1 to 6 months of incubation. This result agrees well with the reported previously of Minori Kanno and Masao Yoshida (2009), they recognized that the decomposition of HA of Paraguay soil followed an increase H/C and O/C ratio during the decomposition process of HA under 30°C from 1 to 9 months of incubation. The O/C ratio is also a representative of the degree of humification. A decrease of this ratio commonly suggests an increase in the aromatic condensation. The value of H/C ratios show the degree of maturity in humic substances (Gonzales-Villa *et al.*, 1992, 2000) since indirectly it reflects the existence of more condensed aromatic ring or substituted ring structure [3]. Therefore, a decrease in atomic H/C and O/C at most of soils studying proved that application of zeolite can resist the decomposition of organic matter.

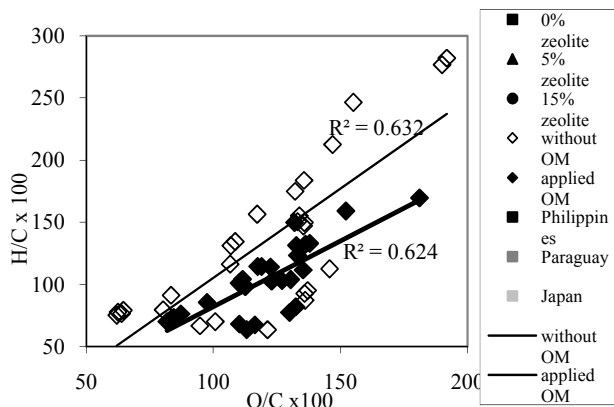


Fig. 6 Atomic H/C versus O/C during the process of humic acid decomposition in soil studying

In addition, through elemental composition value of C, H, N, the degree of unsaturation (DUS) was calculated. DUS of treatments without zeolite was decreased, conversely, an increase at treatments applied zeolite were observed. It showed that HA were condensed by zeolite combine with

humic substances (HS) that could be difficult in cut HA structure during decomposition process of HS (Fig.7).

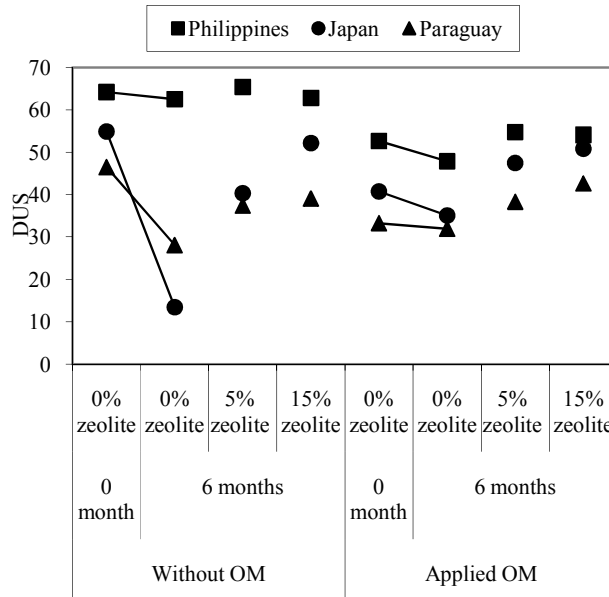


Fig. 7 Changes in Degree of unsaturation (DUS) of humic acids after 6 months of incubation

IV. CONCLUSION

We found that the carbon accumulation of humic fractions as well as the degrees of humification and aromaticity of HA increase by the application Ca-zeolite to the soil. These results affirmed that there are a complexation between oxy of zeolite components and organic acid that take form organo-metallic. And this complexes made the humic acid decomposition process such as oxidation, decarboxylation and demethanation will happen slower than the humic acid decomposition process of the soil without zeolite. These results proved that soil amendment with Ca-zeolite could resist the decomposition of organic matter under high temperature. In addition, we recognized that there were not only tropical soil (Philippines and Paraguay) but also subtropical soil (Japan) have been affected on the decomposition of soil organic matter by global warming.

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REFERENCES

- [1] Baranciková, G., N. Senesi and G. Brunetti. "Chemical and spectroscopic characterization of humic acids isolated from different Slovak soil type,," *Geoderma*, 78: 251-266, 1997.
- [2] Colella C. "Ion exchange equilibria in zeolite minerals," *Mineralium Deposita*, 31: 554-562, 1996.
- [3] Gonzales-Vila, F.J., F. Martin, C. Del Rioj and R. Frund. "Structure characteristics and geochemical significance of humic acids isolated from three Spanish lignite deposit,," *Science of The Total Environment*, 117-118: 335-343, 1992.

- [4] Kumada K.. “ Chemistry of Soil organic matter,” Elsevier, Amsterdam: 241, 1987.
- [5] Kumada, K., O. Sato, Y. Ohsumi and S. Ohta. “Humus composition of mountain soils in central Japan with special reference to the distribution of P type humic acid,” *Soil Science and Plant Nutrition*, 13: 151-158, 1967.
- [6] Ming, DW and Boettingger, J.L.. “Zeolites in soil environments. In: D.L.Bish & D.W.Ming (ed.) *Natural Zeolites: Occurrence, Properties, Applications, Reviews in Mineralogy & Geochemistry*,” Mineralogical Society of America & Geochemical Society, Washington DC, 45: 323-345, 2001.
- [7] Polat, E., M. Karaca, H. Demir and A. Naci-Onus. “ Use of natural zeolite (clinoptilolite) in agriculture,” *Journal of Fruit Ornamental and Plant research*, 12: 183-189, 2004.
- [8] Richard, T., J. Conant, Megan Steinweg, L. Haddix Michelle, A.Paul Eldor, F.Plante Alain and Six.Johan. “ Experimental warming shows that decomposition temperature sensitivity increases with soil organic matter recalcitrance,” *Ecology*, 89 (9): 2384-2391, 2008.
- [9] Ross, S.. “ Organic matter in tropical soils: current conditions, concerns and prospects for conservation,” *Progress in Physical Geography*, 17: 265-305, 1993.
- [10] Schimel, D.S., B. H. Braswell, E. Holland, R. McKeown, D.S. Ojima, T. H. Painter, W. J. Parton and A. R. Townsend. “Climatic, Edaphic, and Biotic Controls Over Storage and Turnover of Carbon in Soils,” *Global Biogeochem. Cycles*, 8 (3): 279-294, 1994.
- [11] Yoshida, M., K. Sakagami, R. Hamada and T. Kurobe. “Studies on the properties of organic matter in buried humic horizon derived from volcanic ash. I. Humus composition of buried humic horizons,” *Soil Science and Plant Nutrition*, 24 (2): 277-287, 1978.