วารสารเกษตร 7(3) : 298-313 (2534)

Journal of Agriculture 7(3) : 298-313 (1991)

SUPPRESSING EFFECT OF METAL IONS ON DECOMPOSITION OF ORGANIC FERTILIZER BY FORMING METAL-ORGANIC COMPLEXES

Patcharee Saenjan [1], Duangsamorn Taja [2], and Hidenori Wada [2]

อิทธิพลของโลหะในการยับยั้งการสลายตัวของปุ๋ยอินทรีย์โดยการเกิดสารประกอบเชิงซ้อนอินทรีย์โลหะ

พัชรี แสนจันทร์ [1], ดวงสมร เตจา [2], และฮิเดโนริ วาดะ [2]

บทคัดย่อ: ศึกษาอิทธิพลของสารประกอบโลหะที่มีต่อการสลายตัวของปุ๋ยอินทรีย์ โดยทดลองกับมูลควายเพราะเป็นปุ๋ยคอกที่ใช้ปรับปรุงบำรุงดินกันอย่างแพร่หลายในเขตร้อน สารประกอบโลหะที่ใช้ได้แก่ Polyhydroxy Al chloride (PAC), $AlCl_3$ และ $FeSO_4.7H_2O$ ส่วนผสมของมูลควายและสารประกอบโลหะถูกบ่มภายใต้สภาพที่มีออกซิเจนเป็นเวลา 0 ถึง 3 สัปดาห์ ทำการวัดคาร์บอนไดออกไซด์ที่ถูกปลดปล่อยออกจากมูลควาย วัดปริมาณ Al, Fe, pH และความหนาแน่นแสง (OD) ในสารละลายมูลควายที่สกัดด้วย KCl และทำการแยกส่วนของสารประกอบอินทรีย์โลหะในสารละลายที่สกัดด้วย KCl และในสารละลายที่สกัดด้วยน้ำ ผลการทดลองชี้ให้เห็นว่าสารประกอบโลหะสามารถลดการสลายตัวของมูลควาย โดยเกิดการสร้างสารประกอบเชิงซ้อนอินทรีย์โลหะ ซึ่งเป็น Polyhydroxy Al และ Fe ที่เกาะกับสารประกอบฮิวมิกและฟุลวิกในมูลควาย

ABSTRACT: Decomposition of organic fertilizer was examined by addition of metal compound. Partially humified buffalo dung (BD) was tested as it is a popular soil amendment in tropical region. Metal compounds used were polyhydroxy Al chloride (PAC), $AlCl_3$ and $FeSO_4.7H_2O$. Mixture of BD and metal compound was incubated under aerobic condition. At appropriate period, carbon dioxide emitted from BD, amount of Al and Fe, pH and optical density in HCl-BD extract and fractionation of metal organic substances in KCl and water extract were analyzed. The results showed that addition of metal compound slightly decreased decomposition of BD through formation of metal organic complexes. The added Al and Fe ions were expected to exist in form of polyhydroxy Al and Fe mainly combined with humic substances of BD.

---

[1] ภาควิชาปฐพีศาสตร์, คณะเกษตรศาสตร์, มหาวิทยาลัยขอนแก่น, 40002.
[1] Department of Soil Science, Faculty of Agriculture, Khon Kaen University, Khon Kaen, 40002, Thailand.
[2] ศูนย์วิจัยศึกษาค้นคว้าเกษตรภาคตะวันออกเฉียงเหนือ, คณะเกษตรศาสตร์, มหาวิทยาลัยขอนแก่น, 40002.
[2] Research Annex, Faculty of Agriculture, Khon Kaen University, Khon Kaen, 40002, Thailand.

INTRODUCTION

Microbial decomposition of organic matter in soil has been studied for many years and a lot of information on this topic have been obtained. However, techniques to control this process succeeded only to a limited degree. The most popular techniques to enhance the microbial decomposition of soil organic matter were air-drying pretreatment (Shioiri, 1940) and increase in soil temperature during the process.

Soil organic matter content is usually much lower in tropical regions than in temperate regions because of rapid oxidation of organic residues (Jenny, 1980). This fact has been ascribed to higher temperature in the former regions than in the latter regions (Jenny and Raychaudhuri, 1960). The low soil organic matter content, in turn, has been considered as main cause of low fertility of the tropical soils. Actually, virgin soils in tropical regions are often rich in organic matter and are degraded when they are cultivated (Kalpage, 1974). Application of organic matter to soil has not been always succesful to restore fertility through increase of organic matter content in the tropical sandy soils. This failure has been suspected to be caused by rapid decomposition of the applied organic matter in the tropical soil.

Sanchez (1976) suggested that some tropical soils with high organic matter contents may be formed by strong interaction of organic matter with iron and aluminum hydroxyoxides and with allophane. The strong interaction could stabilize the soil organic matter against microbial decay.

Recently, new approaches have been made to suppress microbial decomposition of organic matter in the soil. One of them is utilization of matallic ions which have high ability to combine with humic substances in soil. Kubota *et al.* (1986) demonstrated that Al ions, especially polyhydroxy Al ion, could clearly suppress microbial decomposition of well matured (humified) compost. Wada, Kito, Tsuji and Fukushima (1989) obtained similar results though simple Al ion was found to be more effective than polyhydroxy Al ion in suppressing microbial decomposition of well rotted (humified) debris of *Eularia.*

On the basis of above mentioned considerations, we began a series of experiments of find out the technique to suppress microbial decomposition of organic matter in the hope to find a mean to increase organic matter content in sandy soil of the Northeast Thailand.

In the present paper, we examined the following 3 points. 1) could the matallic ions suppress microbial decomposition of buffalo dung, a partially humified organic amendment, which was popular in Northeast Thailand? 2) How effective Al and Fe ions in suppressing microbial decomposition of the buffalo dung? 3) Did the metallic cations really strongly combine with organic compounds of the buffalo dung?

MATERIALS AND METHODS

Buffalo dung (BD) : Fresh BD was collected. It was air dried and passed through a 2 mm seive. Its chemical properties were 21.16 %C, 1.01 %N, C/N = 21.35, 0.15 % P, 0.15 %Mg, 2.08 %K, 0.05 %Na, 9.5 ppm KCl-extractable Al, 2.0 ppm KCl-extractable Fe, pH 8.0 (1:2.5) and cation exchanged capacity (CEC) = 27.78 meq/ 100 g.

Metal compounds : PAC (Polyhydroxyaluminium chloride), $AlCl_3$ and $FeSO_4.7H_2O$ were used as sources of ions of Al and Fe.

Incubation : Each 5 g subsample of the air dried BD was placed in a 500 ml Erlenmeyer flask and was saturated with water solution of a metal compound and well mixed. The amount of the added metal compound was adjusted to saturate cation exchange site of the BD with the simple metal ion: 248 mg Al/100 g BD and 514.7 mg Fe/100 g BD. The flask was tightly closed with a rubber bung from which a small vial containing 5 ml of 2 N NaOH solution was hung with a piece of wire and was placed in an incubator at 37 °C for certain periods : 3, 7, 14 and 28 days. Erlenmeyer flasks without BD were incubated in the same way and regarded as blanks. All plots were duplicated.

Measurement of CO_2 : After each incubation period, the NaOH solution in the vial was added with $BaCl_2$ solution to precipitate CO_2 and the remaining NaOH was titrated with 1 N HCl. The amount of CO_2 evolved from the BD was calculated from the differences in the amount of HCl.

Al and Fe determination : After termination of incubation, the Buffalo dung was shaking for 30 min with 1 N KCl at the ratio of 1:10. The KCl-extract was measured for Al and Fe by using plasma emission spectrometer (Shimadzu ICPA-50) and atomic absorption (Shimadzu AA-670), respectively.

pH and optical density : The KCl extract was measured for pH and optical density (OD) at 400 nm by using a pH meter (TOA HM-20S) and a spectrophotometer (Shimadzu UV-240), respectively. Measurement of OD at 400 nm was modified from the method used by Kumada (1985) and Drijber and Lowe (1989).

Fractionation for metal organic complexes : The KCl extract from BD of 3 day incubation was fractionated. Five milliliters of KCl extract was fed on Sephadex (G-50) column of 1.2 mm diameter 19 cm height. The metal-organic compound was eluted with distilled water and every 5 ml was collected in 10 test tubes. The amount of Al and Fe in each test tube was measured by using the above mentioned equipment. The optical density at 400 nm of the leachate in each tube was also measured.

Water-extract from BD of 3 days incubation (1:10) was also fractionated in the same way.

RESULTS AND DISCUSSION

CO_2 Production from Buffalo Dung as Affected by Metal Compounds (Figure 1.)

Time course of CO_2 emission showed that, in general, its rate increased rapidly during the initial period of 3 days, became slow at 1 week incubation more or less constant afterward.

Metal compound were found to suppress CO_2 production slightly during the first 3 days. This became evident at 1 week incubation and then gradually less remarkable. Among the metal compounds, $AlCl_3$ was the most effective followed by $FeSO_4.7H_2O$ and polyhydroxy Al chloride (PAC).

Thus, the metalic compounds were confirmed to have ability in suppression of BD, though the suppressing effect for BD was not so remarkable as that for the well humified compost (Kobota et al., 1986).

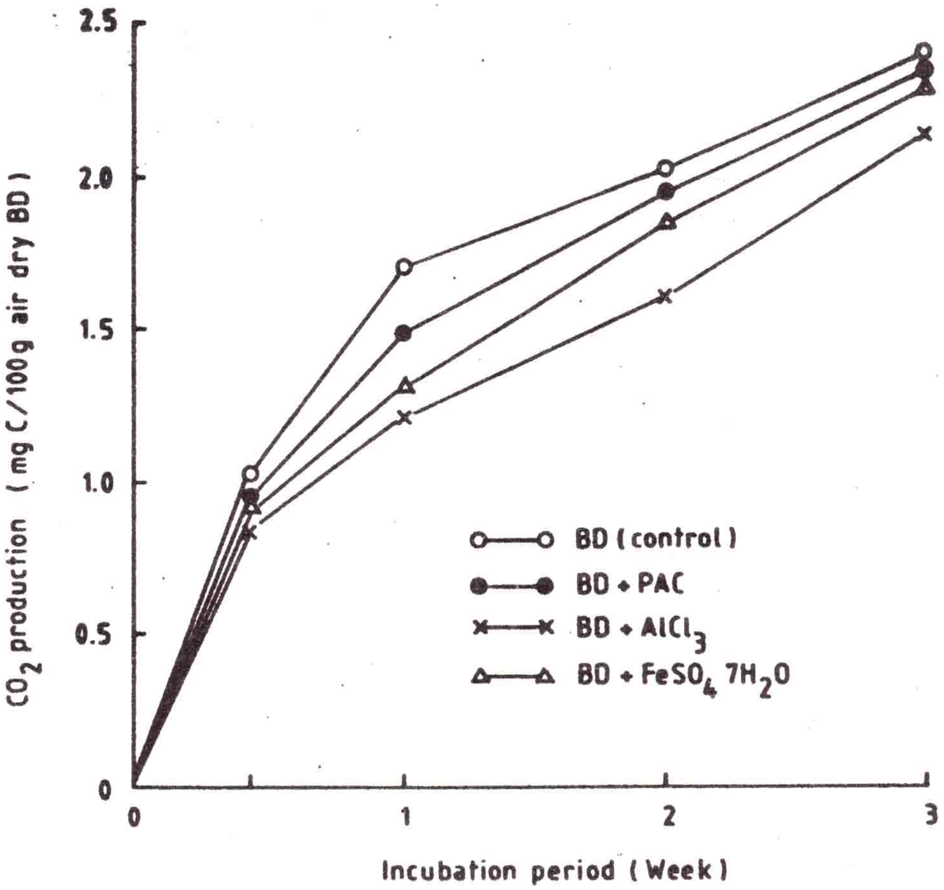

Figure 1. CO_2 production from incubated buffalo dung receiving metal compound

On the basis of Garrett' concept (Garrett, 1951), the reasons for the suppressing effect can be supposed as follows:

(1) Soon after incubation, when water-soluble good organic substrates such as glucose were mainly decomposed by microorganisms. The metallic compounds only slightly suppressed their decomposition, because metal-organic complexes were hardly formed.

(2) At about 1-2 weeks after incubation, less digestible organic substrates like hemicellulose were utilized by microorganisms. The metallic compounds combined with there organic compounds to some degree so that CO_2 production was clearly suppressed.

(3) More than 3 weeks after incubation, cellulose was a main organic substrate. The metal compounds were not effective in suppressing its decomposition, because cellulose was not a suitable compound to form coordinate bond.

pH of buffalo dung-KCl extract (Figure 2.)

In the control plot, pH of the KCl-extract was about 7.7 at the start and slightly increased with time, probably due to decomposition of dissociated acidic organic constituents of BD. Addition of PAC of $FeSO_4.7H_2O$ did not lower the initial pH but somewhat suppressed the increase in pH during incubation. This may be caused by gradual hydrolysis of the metal ions and bondage of the metal ions with undissociated acidic functional groups of organic constituents of BD. Addition of $AlCl_3$ did lowered the initial pH to about 7.5 and strongly suppressed the increase in pH during incubation. This must be a reflection of the fact that $AlCl_3$ is stronger acid than the other metallic compounds.

Futhermore, pH of all the KCl-extracts indicated: (1) monomeric metallic ions could not exist both in the KCl-extract and in BD. (2) Fe^{2+} contained in $FeSO_4.7H_2O$ was quickly oxidized to Fe^{3+} which was subjected to hydrolysis.

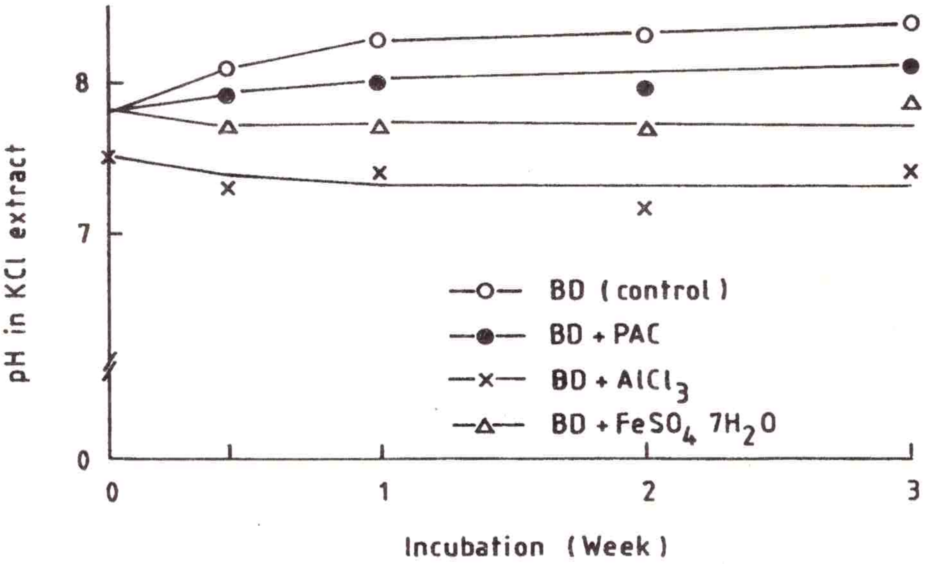

Figure 2. Change in pH of incubated buffalo dung receiving metal compound.

KCl-extractable Al (Figure 3.)

Figure 3 shows that the amount of the KCl-extractable Al was small at the start and slightly decreased with time both for the control plot and for the $FeSO_4.7H_2O$ plot.

On the contrary, the amount of the KCl-extractable Al was remarkable large at the start, rapidly decreased in a short period and then gradually decreased afterward for PAC plot and $AlCl_3$ plot. This must be resulted from hydrolysis of Al ions and binding the hydrolyzed Al with the functional groups. That is, a large part of the hydrolyzed Al itself and/or its coordinated compounds with organic constituents of BD were unextractable with the KCl solution.

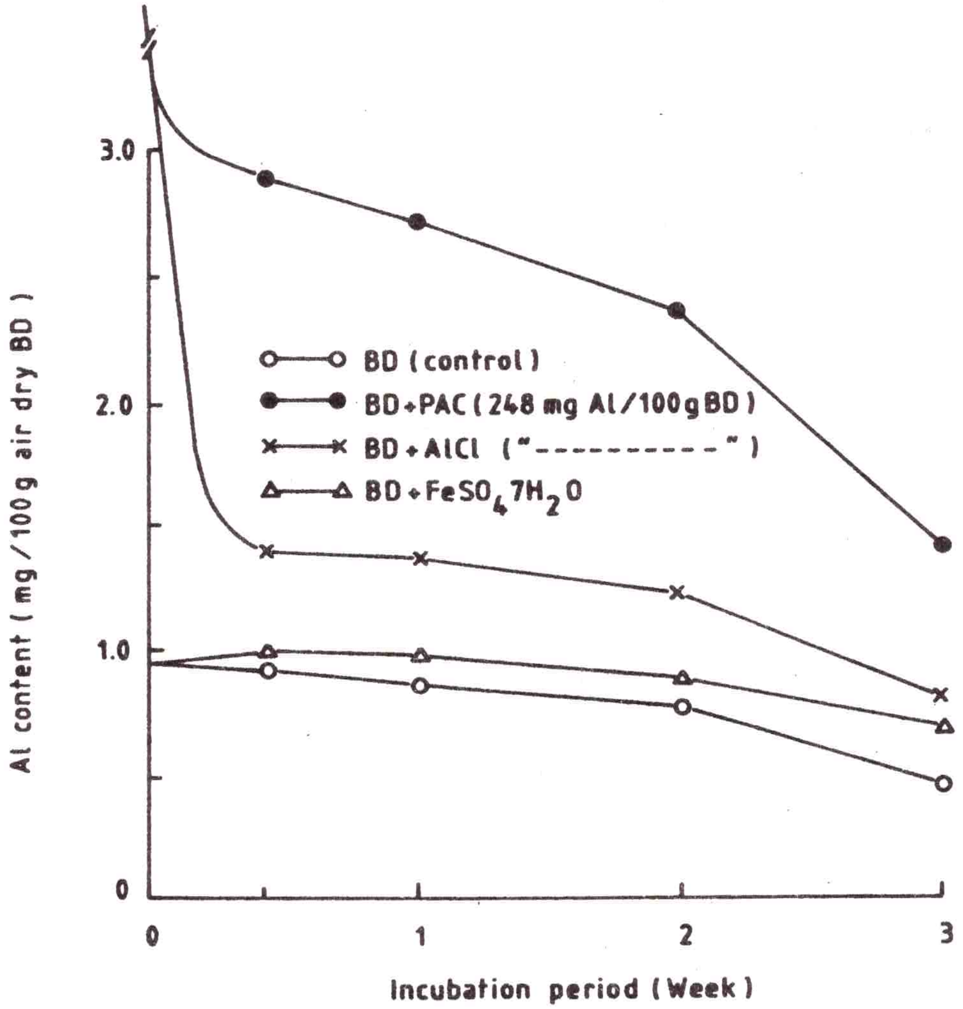

Figure 3. Al content in incubated buffalo dung (BD) receiving metal compound.

KCl Extractable Fe (Figure 4.)

In the control plot and the PAC plot, the amount of KCl-extractable Fe gradually increased with time. This Fe must be coordinated with **water-soluble humic substances** whose amount usually increased when organic materials were humified (Wada, 1963). On the contrary, in the $FeSO_4$ plot, the amount of KCl-extractable Fe was very large at the start, sharply decreased within a short period and remained more or less constant at low level. This suggested that hydrolyzed products of Fe was difficult to be extracted with KCl and that organic compounds coordinated with the hydrolyzed products of Fe were also difficult to be extracted with KCl.

In the case of the $AlCl_3$, the amount of KCl-extractable Fe decreased with time and almost unstable a few weeks after incubation. This may be resulted from that the hydrolyzed products of Al ($AlCl_3$) made the **water-soluble humic substances** insoluble so that the amount of KCl-extractable Fe could not increase.

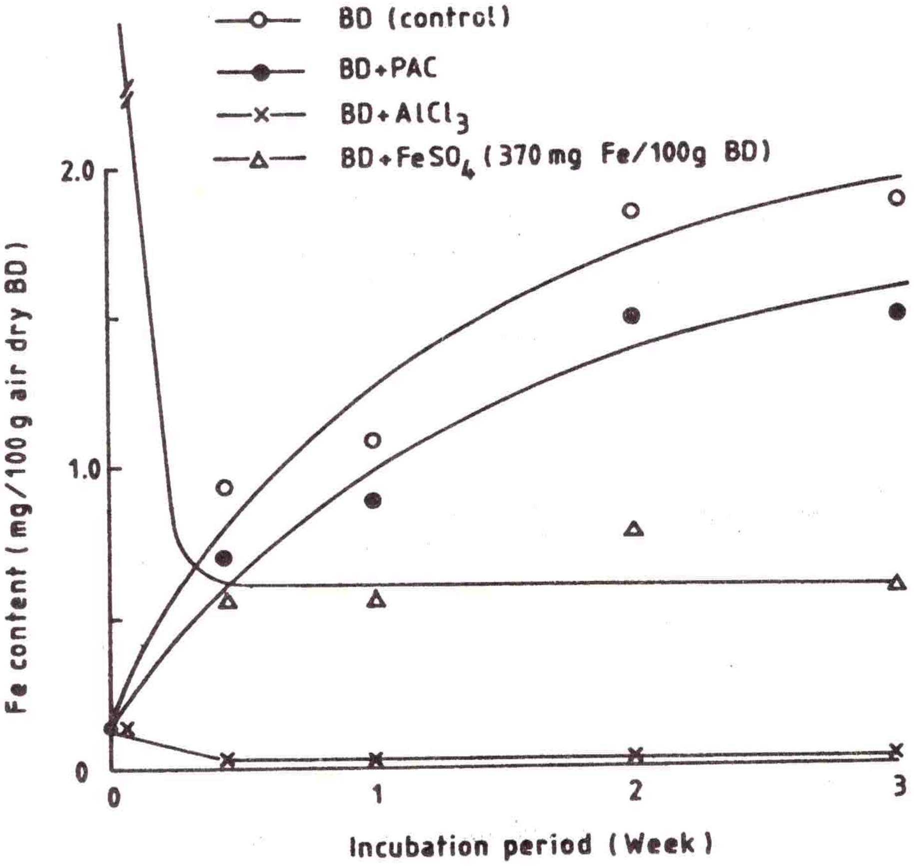

Figure 4. Fe content in Incubated buffalo dung (BD) receiving metal compound.

KCl-extractable Humic Substances (Figure 5)

The amount of KCl-extractable humic substraces was estimated by OD at 400 nm. This OD decreased rapidly and remained stable in the following order: control plot > PAC plot > $AlCl_3$ plot > $FeSO_4.7H_2O$ plot. Furthermore, these results were in good agreement with those mentioned above.

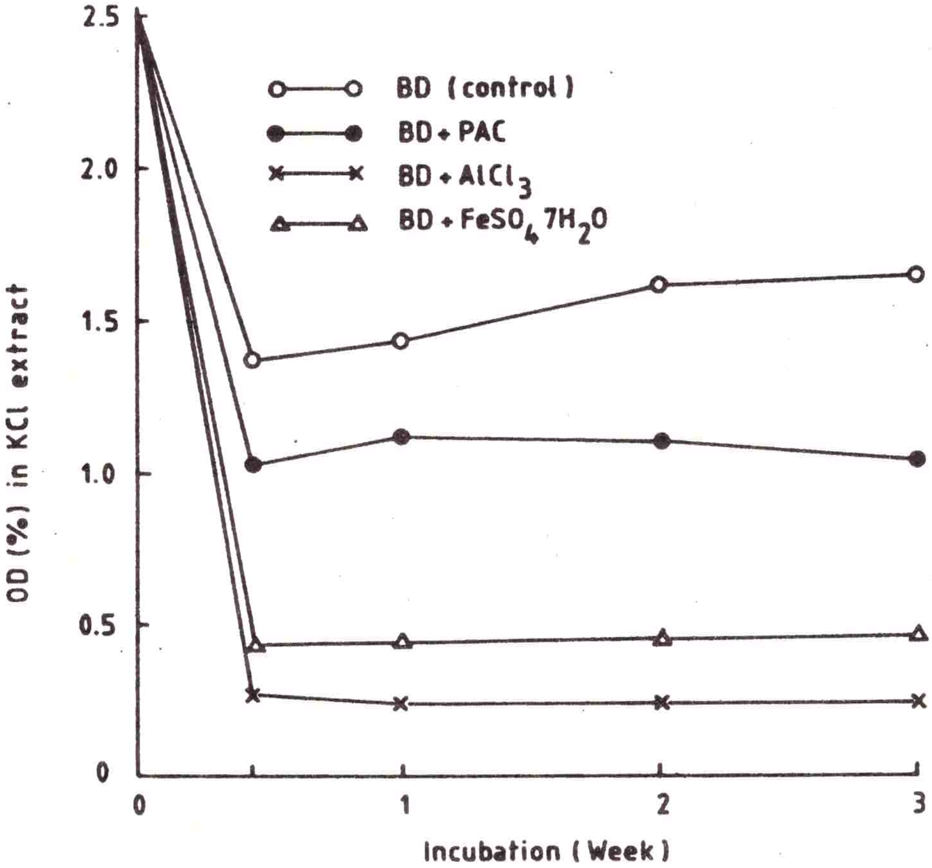

Figure 5. Optical density (OD) in buffalo dung (BD) - KCl extract. BD received various metal compounds.

Fractionation of KCl Extract Using Sephadex Column (Figure 6.)

In the control plot, the OD at 400 nm had 2 peaks, the first peak being higher than the second peak (Figure 6a). The peak of Al in control plot appeared at the second peak but not at the first peak. This suggested that KCl-extractable humic substances in buffalo dung was consisted of rather higher molecular weight fraction and low molecular weight fraction, the former being predominating over the latter. In addition, most of KCl-extracable Al was considered to be combined with the low molecular weight fraction.

Addition of PAC did not affect both the amount and the distribution pattern of molecular weight of the KCl-extractable humic substances (Figure 6b). However, the amount of KCl-extractable Al remarkably increased in both the high molecular weight and the low molecular weight fractions.

In the $AlCl_3$ plot, OD at 400 nm much lower than that in the control plot (Figure 6c) suggested humic substances was hardly extracted with the KCl solution in the presence of $AlCl_3$. This was especially remarkable for the high molecular fraction. Elution pattern of Al was similar to that of humic substances. These results suggested that in the presence of $AlCl_3$ the hydrolysis products of $AlCl_3$ were effectively flocculated the **water-soluble humic substances.**

Addition of $FeSO_4$ had similar effect on the amount of KCl-extractable humic substances as that of $AlCl_3$ (Figure 6d). The amount and the distribution pattern of KCl-extractable Fe was also similar to those of KCl-extractable Al mentioned above. These results suggested that in the initial period of incubation, strength of bondage between humic substances and metal ions was decreased in the following order: $AlCl_3 = FeSO_4 > PAC$.

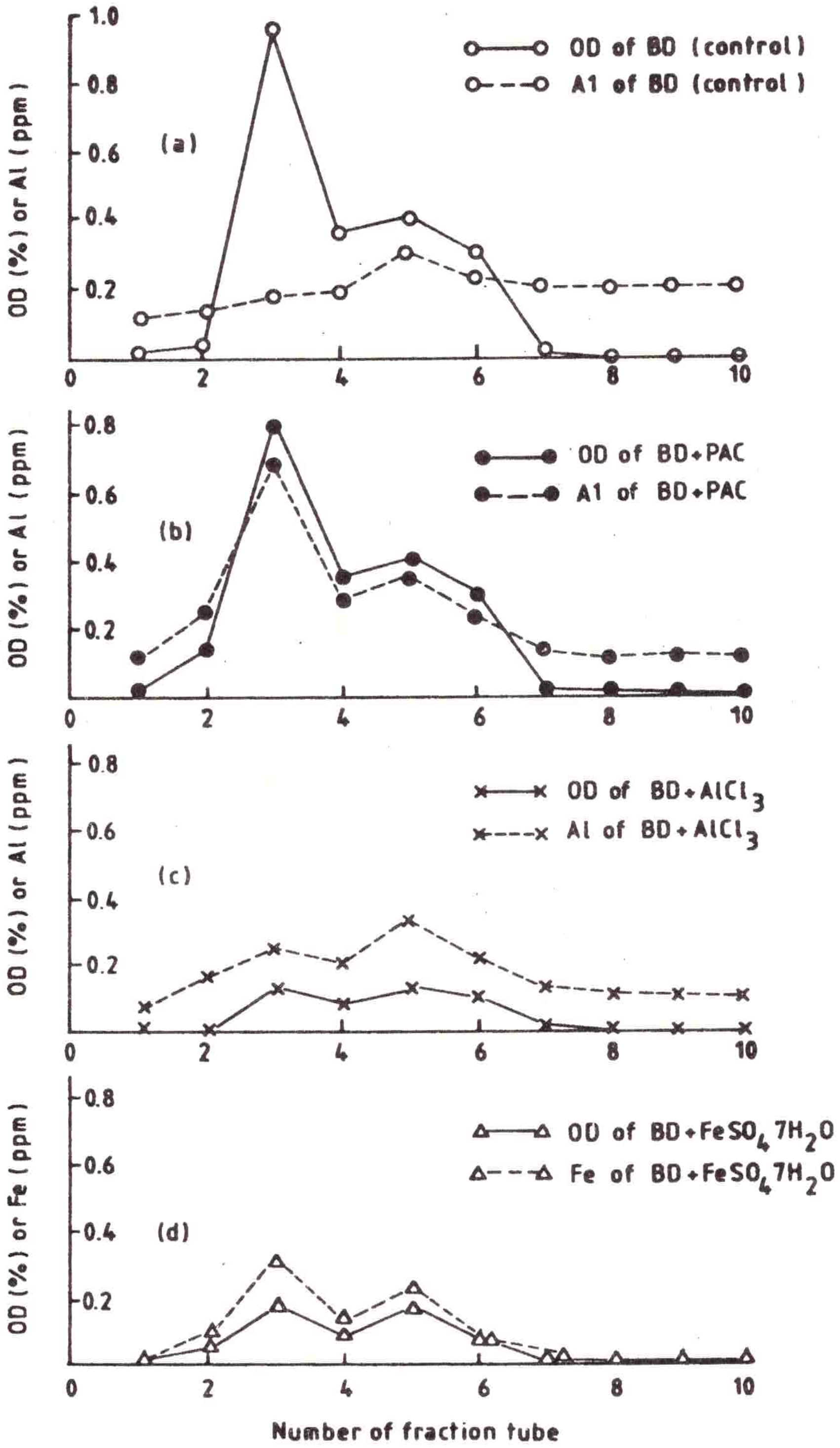

Figure 6. Optical density and metal content in BD-KCl extract BD was incubated with metal compound for 3 days before fractionated through Sephadex G-50.

Fractionation of Water Extract Using Sephadex Column (Figure 7)

To confirm formation of metal ion-humic substances complexes, the 3-day incubation samples were extracted with water. All the water-extract were examined for distribution pattern of molecular weight of humic substances and contents of metal ions in each fractions in the same was as the KCl-extract.

As for buffalo dung, the amount of humic substances was larger and molecular weight was smaller in the water-extractable humic substances than in the KCl-extractable humic substances (Figure 7a). This implied that the water-soluble humic substances were coagulated to some degree with KCl.

PAC somewhat decreased the amount of the water-soluble humic substances (Figure 7b). This may be caused by precipitation of a part of the original water-soluble humic substances with PAC. Most of the water-soluble Al was contained in the high molecular weight fraction. Probably, only a small part of the added PAC combined the original water-soluble humic substances.

$AlCl_3$ remarkable decreased the amount of the water-soluble humic substances and the amount of the water-soluble Al was low (Figure 7c). This must be a reflection of that bondage between humic substances and Al was abundantly formed and the water-soluble humic substances was more or less completely precipitated by addition $AlCl_3$.

The amount of the water-soluble humic substances was decreased with $FeSO_4$ in a similar way as with PAC, though the high molecular weight fraction was less decreased with $FeSO_4 \cdot 7H_2O$ than with PAC (Figure 7d). A rather large amount of water-soluble Fe was included in the high molecular weight fraction. These results suggested : (1) formation of bondage between the humic substances and Fe was not abundant, and (2) some water-soluble non-humic substances protect Fe-hydroxide colloid against precipitation.

These results were in good agreement with those mentioned above.

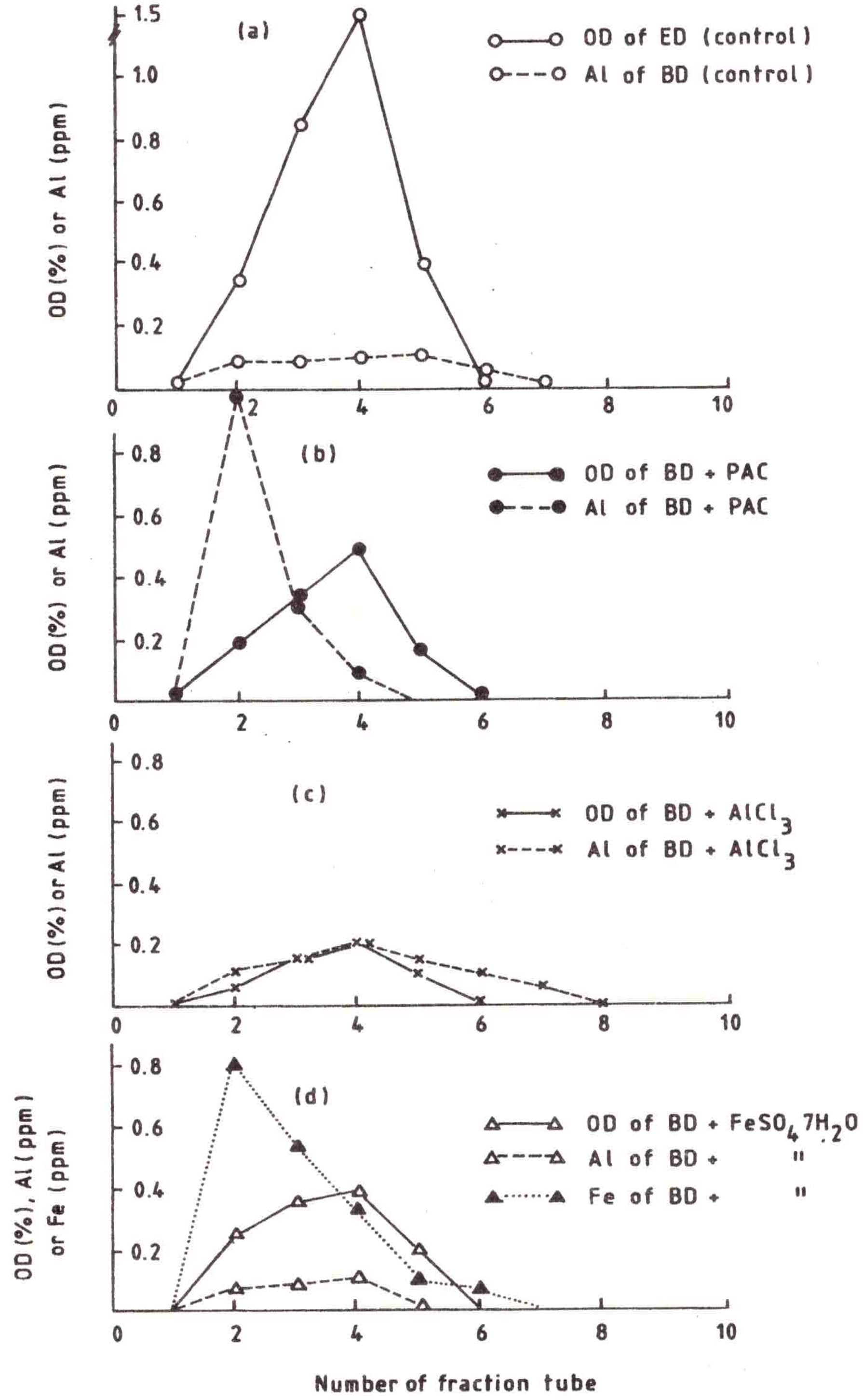

Figure 7. Optical density and metal content in BD-H_2O extract. BD was incubated with metal compound for 3 days before fractionated through Sephadex G-50.

GENERAL DISCUSSION

The present experiments demonstrated that Al and even Fe compounds had ability to suppress microbial decomposition of buffalo dung, only weakly humified plant debris. The suppressing effects of these metallic ions for buffalo dung were less remarkable than those reported previously for well humified organic debris by Kobota and Wada (1977).

Stevenson and Ardakahi (1972) wrote that evidence for complex formation and chelation by humic substances has been based upon the inability of exchangeable cations such as K to replace adsorbed micronutrients. The present experiment shows coincident result that both Al and Fe ions can combine with organic compounds of buffalo dung.

Formation of strong between metallic ions and functional groups of organic compounds must be a prerequisite of protecting the organic compounds against microbial attack. The functional groups, site of microbial attack, are blocked by being combined with metallic ions.

As for formation of strong bond between metallic ions and humic substances, as early as 1931, McGeoge observed divalent cations were more tightly held by humic acid than monovalent cations. Schitzer and Skinner (1963 a, b) found that Al which was combined with organic matter was hydroxylated and had average composition of $Al(OH)^{2+}$.

This is natural, because metallic ions must be strongly combined with organic substrates for suppressing their microbial decomposition.

CONCLUSION

The present experiment manifested that Al and Fe compounds could suppress microbial decomposition of buffalo dung to a certain extent through formation of metal organic complexes. Amoung metal compounds, the suppressing effect decreased in the following order : $AlCl_3 > FeSO_4.7H_2O$ > PAC. Bondage between metal ions may be very weak for the water-soluble organic compounds, somewhat strong for the hemicellulose-type organic compounds and weak for microbial debris.

Formation of metal organic complexes was suggested to be polyhydroxy Al and polyhydroxy Fe combined with humic substances exist in buffalo dung. We hope that the above results can be applied to stabilize soil organic matter in tropical region. However, further research in various kinds of organic matter and of metal compound should be conducted in a similar manner and expecially to infertile tropical soils of low organic matter content.

REFERENCES

Alexander, M. (1977). Introduction to Soil Microbialogy. John Wiley & Sons, New York.

Bohn, H.L., McNeal, B.L. and O'Connor, G. A. (1985). Soil Chemistry. John Willey & Sons, New York.

Drijber, R.A. and Lowe, L.E. (1990). Nature of humus in Andosols under differing vegetation in the Sierra Nevada, Mexico. Gederma. 47 : 221-231.

Frimmel, F.H. and Christman, R.F. (1988). Humic Substances and Their Rile in the Environment. John Wiley & Sons, New York.

Garrett, S.D. (1951). Ecological groups of soil fungi; a survey of substrate relationships. New Phytol. 50 : 149-166.

Gray, T.R.G. and Wiloliams, S.T. (1977). Soil micro-organisms. Longman, London and New York.

Jenny, H. and Raychaudhuri, S.P. (1960). Effect of Climate and Cultivation on Nitrogen and Organic Matter Reserves in Indian Soils. Ind. Council Agr. Res., New Delhi.

Jenny, H. (1980). Ecological Studies 37. The Soil Resource. Springer-Verlag. New York, Heidelberg, Berlin.

Kuboto, T. and Wada, K. (1977). Size fraction, dissolution analysis. and infrared spectroscopy of humus complexes in ando soil, J. Sci Soil Manure Jpn. 155-160 p. (In Japanese)

Kalpage, F.S.C.P. (1974). Tropical Soils St. Martin's Press, New York.

Kumada, K. (1985). Elementary Composition and Absorption Spectra of Humic and Fulvic Acids. Soil Sci. Plant. Nutr. 31(3) : 437-448.

McGeoge, W.T. (1931). Organic compound associated with base exchange reactions iun soils. Arizona Agric. Exp. Stn. Tech. Bull. 31.

Ritnam, H.D. & Schmidt, E.L. (1959). Studies on the free amino acid fraction of soils. Soil Sci. 87 : 22-27.

Schnitzer, M. and Skinner S.I.M. (1963a). Organo-metallic interaction in soils : 1. Reaction between a number of metal ions and organic matter of a podozol Bh horizon. Soil Sci. 96 : 89-93.

Schnitzer, M. and Skinner, S.I.M. (1963b) Organo-metallic interaction in soils : 2 Reactions between different forms of iron Sand Sluminum and organic matter of podzol Bh horizon. Soil Sci. 96 : 181-186.

Shioiri, M. and Aomine, S. (1940). The effect fo drying the paddy soil before drying. In : Special Report of Agricultural Experiment Station.

Stevenson, F.J. and Ardakani, M.S. (1972). Organic Matter Reactions Involving Micronutrients in Soils. In : Micronutrients in Agriculture. Mortvedt, J.J., Giordano, P.M., Lindsay, W.L. (eds.). Soil Science Society of America, Madison.

Wada, H. (1963). Effects of application of compost on the properties of soil organic matter (in Japanese). Ph.D. thesis, The University of Tokyo, Japan.

Wada, H., Kito, T., Tsuji, H. and Fukushima, T. (1989). Selection of effective reagent to suppress decomposition of reed debris (part 1 and 2). Proceedings of 16th Congress of Nippon Bokin Bobai Gakkai p. 63 and 64.

Watanabe, I. (1984). Anaerobic decomposition of organic matter in flooded soils. In : Organic Matter and Rice. International Rice Research Institute. Los Bayos, The Philipines. pp 237-258.