

Changes of Some Organic Acids in the Hydrolysates of Decomposing Litters of Wild Grasses and Tree Leaves

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短 報

腐熟過程中 落葉類 加水分解物의 有機酸含量 變化

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SUMMARY

Changes in the concentrations of six low-molecular-weight organic acids extracted from hydrolysates of plant residues undergoing decomposition for 90 days under the laboratory condition were investigated.

1. Litters of deciduous and coniferous trees and wild grass cuttings were sampled for the study and concentrations of formic, acetic, succinic, tartaric, malic and citric acids were determined. The concentration of malic acid were negligible.

2. In the wild grass cuttings, the total concentration of low-molecular-weight organic acids decreased with the passage of decomposition. Monocarboxylic acids, i. e., formic and acetic acids, predominated over dicarboxylic and tricarboxylic acids. Formic and acetic acids appeared to be compensatory for each other. Concentration of citric acid increased at a remarkable rate.

3. The total concentration of organic acids in the hydrolysates of deciduous litter was shown to increase. The concentration of monocarboxylic acids was significantly higher in the end of the period of decomposition. Here again a compensatory relationship was observed between concentrations of formic and acetic acids.

4. There was comparatively little change exhibited during the period of experiment concerning the concentrations of organic acids from hydrolysates of decomposing coniferous litter. In contrast with the others, however, the concentration of succinic acid, a dicarboxylic acid, maintained the highest level.

INTRODUCTION

Aqueous extracts of forest litters were observed always to contain some low-molecular-weight organic acids^{13,14}. The organic acids were believed to be present in association with humic and fulvic acids. They may be either physically adsorbed or chemically bonded¹⁴. In most mineral soils low-molecular-weight acids, such as formic, acetic, oxalic, and butyric acids, have been identified to oc-

cur^{1,3,12,13,14}. Long-chain aliphatic acids have been known to persist for a considerable period of time mainly due to their low solubility and adsorption on clay and humus particles, whereas water-soluble low-molecular-weight organics are likely to have a transitory existence and their relative proportion in soil solutions may be at the highest when plant residues are put under active microbial decomposition^{9,13,20}.

Chelation by organic acids has been known as a

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primarily responsible factor for the solubilization of mineral elements in soils. The decomposition of insoluble phosphates and silicate minerals results in the formation of soluble forms of phosphorus, potassium, calcium, magnesium, and various other trace elements through the action of organic acids^{6, 11, 13)}. Weathering of rocks has been known to be accelerated in the presence of organic acids, and the contribution of which to the mobilization and transport of plant mineral nutrients has drawn a great attention. Evidences have been accumulated to prove their effect on the growth of higher plant^{4, 5, 7, 12, 15, 17, 18, 19)}. Both favorable and unfavorable influences were observed from the increased bio-availability of mineral elements^{13, 15, 16)}.

Considerable variations and erratic fluctuations in the level of low-molecular-weight organic acids are anticipated when plant residues are subjected to microbial attack, which reflect a balance between synthesis and decomposition²⁾. The dynamic status of soil environment should no doubt be greatly influenced in accordance with them.

MATERIALS AND METHODS

1. Plant Materials

Litters of deciduous and coniferous forest trees

and wild grass cuttings were collected separately in the fall. They were air-dried, powdered, and then allowed to decompose in an incubator at $30 \pm 1^\circ\text{C}$ for 0, 45, and 90days, respectively.

2. Method of Analysis

Samples taken at different periods of decomposition were hydrolyzed and contents of organic acids were determined following the method used by Oades et al¹⁹⁾. An HPLC(Wates Model 201) instrument was employed for the analysis of 6 low-molecular-weight organic acids: formic, acetic, succinic, malic, tartaric, and citric acids.

RESULTS AND DISCUSSION

The total molar concentration of low-molecular-weight organic acids increased with the progression of decomposition in the case of wild grass cutting. This trend appeared to be reversed in deciduous litter, while there was no significant change observed in coniferous litter(Table 1). It must be noted that the total concentration of organic acids from wild grass cutting enormously exceeded those from deciduous and coniferous litters. In the end of 90days of decomposition, the hydrolysates of decomposed wild grass cutting co-

Table 1. Content of organic acids in the hydrolysates of decomposing plant residues

Plant materials	Period (d)	Organic acids($\mu\text{mol/g}$ dry matter $\times 10^2$)						Total
		Formic	Acetic	Succinic	Malic	Tartaric	Citric	
Wild grass cutting	0	28838.2	6857.0	380.9	tr	136.1	18.7	36230.8
	45	102.0	15639.6	72.1	tr	6.1	390.2	16209.9
	90	49.5	10390.3	103.3	tr	28.1	520.3	11091.5
Deciduous litter	0	1170.4	339.8	508.3	tr	24.1	40.2	2083.3
	45	1212.0	321.4	632.8	tr	32.5	48.4	2247.0
	90	992.6	3033.5	420.8	tr	25.8	43.6	4516.1
Coniferous litter	0	280.6	329.4	918.7	tr	25.2	24.3	1578.1
	45	226.9	299.7	828.0	tr	4.8	119.2	1478.6
	90	279.5	341.1	948.3	tr	11.9	5.4	1586.1

tr = trace

ntained a total of 110.9 μ mol of organic acids per 1 gram of dry matter, almost 2 times that of deciduous, and 6 times that of coniferous litters, respectively, far exceeding those reported for hydrolysates of grain residues⁷⁾.

The change in the molarity of individual organic acid was in general rather erratic and there was not any consistent fluctuation observed during the given period of decomposition. Only a trace of malic acid was detected in all samples.

The relative molar concentration of acetic acid increased significantly in decomposing wild grass cutting becoming predominant gradually. At the same time the relative molar proportion of formic acid reduced at a drastic rate. It seemed that there was a compensatory relationship existed between formic and acetic acids. Increase of citric acid, a tricarboxylic acid, was remarkable.

There was a steady increase and decrease in molar concentration of acetic and formic acids, respectively in deciduous litter.

Coniferous litter appeared to experience a little change in regard to the concentration of low-molecular-weight organic acids. It may be most likely that coniferous litter is more resistant to microbial degradation than the other plant residues.

In general, the concentration of low-molecular-weight organic acids was the greatest in the hydrolysates of wild grass cutting and the lowest in those of coniferous litter as well recognized¹³⁾. The level of the concentration of succinic acid in coniferous litter remained very high. Monocarboxylic acids(formic plus acetic) constituted the greatest portion of all organic acids in wild grass cutting, which also holds on in deciduous litter. In coniferous litter, the highest level of concentration belongs to succinic acid, a tricarboxylic(Fig. 1).

Isolated water-soluble low-molecular-weight organic acids would be expected to have a short transitory existence in soil¹⁴⁾, but they might be quite persistent when they occur in close associa-

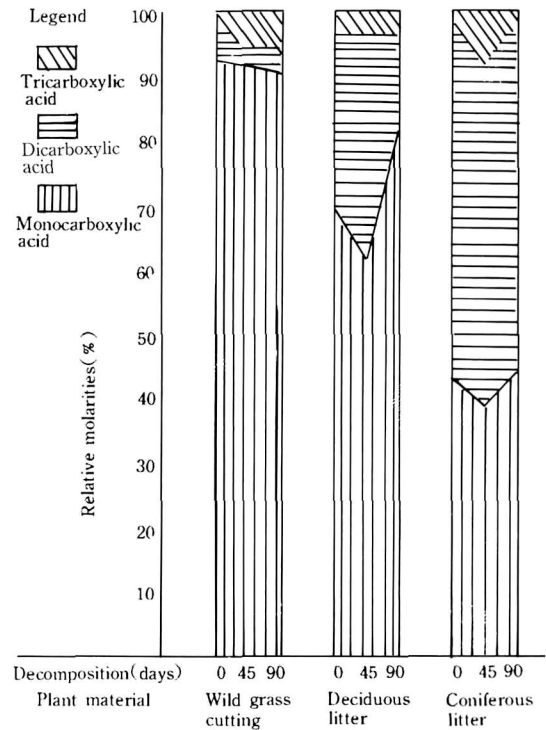


Fig. 1. Changes of relative molarities of organic acids in the hydrolysates of decomposing wild grass, deciduous, and coniferous litter, respectively.

tion with humic and fulvic acid, exerting their influence on the weathering of rocks, solubilization and mobilization of minerals mainly through chelation.

摘 要

山野草,闊葉樹와 針葉樹落葉을 實驗室條件下에서 90日間 腐熟시키면서 經時的으로 試料를 採取하여 酸加水分解시킨후 6個의 低分子量의 有機酸을 分析한 結果는 다음과 같다.

1. Formic, acetic, succinic, malic, tartaric와 citric acid가 檢出되었으며 其中 malic acid는 全試料中에서 極히 微量으로 含有되어 있었다.

2.山野草의 경우 低分子量 有機酸의 濃度는 腐熟期間이 經過함에 따라 減少했으며 formic acid와 acetic acid等 monocarboxylic acid는 dicarboxylic

acid와 tricarboxylic acid에 비해 훨씬 높은 농도를 보였고 formic acid와 acetic acid는 相互補充 關係가 있었다. Citric acid는 腐熟期間이 經過함에 따라 濃도가 增加하였다.

3. 闊葉樹落葉의 경우 腐熟期間이 經過함에 따라 monocarboxylic acid濃도가 相對的으로 높았다. Formic acid와 acetic acid사이는 相互補充 關係가 있음이 究明되었다.

4. 針葉樹落葉의 경우 腐熟期間이 經過함에 따라 有機含有量의 變化가 別로 나타나지 않았다. 山野草와 闊葉樹落葉과는 對照的으로 dicarboxylic acid인 succinic acid濃도가 가장 높았다.

引用文獻

1. Albuizio, A., and G. Ferrari. 1989. Modulation of the Molecular Size of Humic Substances by Organic Acids of the Root Exudates. *Plant and Soil*. 113 : 237~241.
2. Alexander, M. 1977. *Introduction to Soil Microbiology*, 2nd ed. John Wiley and Sons.
3. Flaig, W. 1971. Organic Compounds in Soils. *Soil Sci.* 111 : 19~33.
4. Goh, T. B., and P. M. Huang. 1984. Formation of Hydroxy-Al-Montmorillonite Complexes as Influenced by Citric Acid. *Can. J. Soil Sci.* 64 : 411~421.
5. Goh, T. B., and P. M. Huang. 1986. Influence of Citric and Tannic Acids on Hydroxy-Al-Interlayering in Montmorillonite. *Clays and Clay Minerals*, 34(1) : 37~44.
6. Inoue, K., and P. M. Huang. 1986. Influence of Selected Organic Ligands on the Formation of Allophane and Imogolite. *Soil Sci. Soc. Amer. J.*, 50(6) : 1623~1633.
7. Kim Jeong-Je, Kang-Soon Choi, and Young-Oh Shin. 1991. Changes in the Contents of Some Organic Acids in the Hydrolysates of Decomposing Straws of Rice, Barley, Wheat, and Rye. *J. Korean Soc. Soil Sci. Fert.* 24(4) : 302~305.
8. Kononova, M. M. 1966. *Soil Organic Matter. Its Nature, Its*

Role in Soil Formation and in Soil Fertility. 2nd ed. Pergamon Press.

9. Mortland, M. M. 1986. Mechanisms of Adsorption of Nonhumic Organic Species by Clays. In "Interactions of Soil Minerals with Natural Organics and Microbes". SSSA Spec. Pub. No. 17 : 59~76.
10. Oades, J. M., M. A. Kirkman, and G. H. Wagner. 1970. The Use of Gas-liquid Chromatography for the Determination of Sugars Extracted from Soils by Sulfuric Acid. *Soil Sci. Soc. Amer. Proc.* 34 : 230~235.
11. Schnitzer, M., and S. I. M. Skinner. 1965. Organo-Metallic Interactions in Soils : 4. Carboxylic and Hydroxyl Groups in Organic Matter and Metal Retention. *Soil Sci.* 99 : 278~284.
12. Schwartz, S., Varner J.M and W. Martin, 1954. Separation of Organic Acids from Several Dormant and Incubated Ohio Soils. *Proc. Soil Soc. Amer.* 18 : 174.
13. Stevenson, F. J. 1967. Organic Acids in Soil. In "Soil Biochemistry" ed. by McLaren, A. D., and Peterson, G. H. Marcel Dekker.
14. Stevenson, F. J. 1982. *Humus Chemistry : Genesis, Composition, Reactions*. John Wiley & Sons.
15. Stevenson, F. J., and A. Fitch. 1986. Chemistry of Complexation of Metal Ions with Soil Solution Organics. In "Interactions of Soil Minerals with Natural Organics and Microbes." SSSA Spec. Pub. No. 17 : 29~58.
16. Takijima, Y. 1964. Studies on the Mechanisms of Root Damage of Rice Plants in the Peat Paddy Fields. 1. *Soil Sci. Plant Nutr.* 10 : 231~238.
17. Tan, Kim H. 1986. Degradation of Soil Minerals by Organic Acids. In "Interactions of Soil Minerals with Natural Organics and Microbes." SSSA Spec. Pub. No. 17 : 1~27.
18. Tate, R. L. 1987. *Soil Organic Matter : Biological and Ecological Effects*. John Wiley & Sons.
19. Violante, A., and P. M. Huang. 1984. Nature and Properties of Pseudoboehmites Formed in the Presence of Organic and Inorganic Ligands. *Soil Sci. Soc. Amer. J.* 48 : 1193~1201.
20. Violante, A., and P. M. Huang. 1985. Influence of inorganic and Organic Ligands on the Formation of Aluminium Hydroxides and Oxyhydroxides. *Clays and Clay Minerals*. 33(3) : 181~192.