

toxic substances in stubbles to elucidate the cause of poor growth of successively grown crops. His co-worker Borner (1955, 1956) detected p-hydroxybenzoic acid, p-coumaric acid, and ferulic acid in the straw and stubble of rye, wheat, and barley. The quantitative determination of phenolic acids in soils was accomplished by Whitehead (1964), who found p-hydroxybenzoic acid, vanillic acid, p-coumaric acid, and ferulic acid in 4 soils, each at a concentration lower than 0.05 mM. Phenolic acids have been assumed to be growth inhibitors for dryland crops (Wang et al 1967b), the phytotoxic substances associated with the decomposition of plant residues in anaerobic soil (Patrick 1971), and the cause of phytotoxic effects of decomposing rice residues in soil (Chou and Lin 1976).

Kuwatsuka and Shindo (1973) determined phenolic acids extractable with a methanol-0.1 N NaOH mixture from both fresh rice straw and decomposing rice straw to be p-coumaric, ferulic, p-hydroxybenzoic, and vanillic acids and trace amounts of salicylic, syringic, protocatechonic, -resorcylic, caffeic, sinapic, gallic, and gentisic acids. From the results of incubating rice straw at different temperatures under moist and flooded conditions, Shindo and Kuwatsuka (1975a) assumed that phenolic acids which initially existed in rice straw were rapidly degraded in the early stages of incubation and subsequently produced again

from the lignin component. The pathways from p-coumaric acid to p-hydroxybenzoic acid and from ferulic acid to vanillic acid were deduced from the changes in amounts of these phenolic acids. To alleviate their toxic effects, p-coumaric acid and ferulic acid were also temporarily methylated by soil microbes (Shindo and Kuwatsuka 1975b) and gradually transformed to p-hydroxybenzoic acid and vanillic acid. These latter acids are further transformed via protocatechuic acid to humic substances by polymerization or to aliphatic acids by ring cleavage.

When rice straw was mixed with soil and incubated under moist and flooded conditions, phenolic acids due to rice straw decreased gradually with time. It took nearly 30 days for the amounts of p-coumaric and ferulic acids to decrease to half of their initial levels when the rate of rice straw to soil was 8% (Shindo and Kuwatsuka 1977). After 6-10 weeks of incubation, decreasing curves of p-coumaric and ferulic acids showed shoulders, indicating the formation of these acids in the soil. Phenolic acids decreased more rapidly under moist conditions than under flooded conditions.

Shindo and Kuwatsuka (1978) determined the concentrations of phenolic acids in nine rice soils in Japan as 10-26 ppm (average 21 ppm); the levels were not affected by rice straw incorporated after the preceding cropping season. It seems that phenolic acids at those levels in rice

soils do not affect the growth of either the root or the whole rice plant. Shindo and Kuwatsuka (1976) ascribed the low concentration of phenolic acids in rice soils to leaching. Leaching of phenolic acids in soil profiles is also obvious in the data of Wang et al (1967b).

The kinetics of phenolic acids were investigated by Tsutsuki and Ponnampereuma (unpublished) in three submerged soils treated with 0.25% rice straw, rice straw compost, or green manure at two temperatures (20 and 35°C). The largest concentrations of phenolic acids ranged between 13.6 $\mu\text{mol/kg}$ soil for p-hydroxybenzoic acid and 74.2 $\mu\text{mol/kg}$ soil for ferulic acid when rice straw was applied. Addition of 0.25% green manure or compost affected the concentration of phenolic acids in soils only a little. Changes in the concentrations of phenolic acids in Louisiana clay after 2 and 6 weeks of submergence at 20 and 35°C are shown in Figure 4. After 2 weeks of anaerobic incubation, the concentration of each phenolic acid was always higher at 20°C. However, the difference due to the incubation temperature was small at this time. The concentration of p-hydroxybenzoic acid increased after 6 weeks of incubation at 20°C, while it decreased with time at 35°C. At 35°C, degradation of p-hydroxybenzoic acid may be faster than its formation. Concentrations of the other phenolic acids such as vanillic, p-coumaric, ferulic, and sinapic acids

increased with increased period of incubation at both temperatures. In Luisiana clay, concentrations of phenolic acids were higher at 20°C than at 35°C after 2 and 6 weeks of incubation. However, in Pila clay loam and Maahas clay the concentrations of phenolic acids were higher at 35°C after 6 weeks of incubation. Higher temperature might have favored the formation of phenolic acids from rice straw.

The discussions which consider phenolic acids as plant growth inhibitors in soils are usually based upon the concentration of phenolic acids determined by alkaline extraction, and the amounts of water soluble phenolic acids are very low. The amounts of water soluble phenolic acids in the soil under permanent pasture at pH 5.8 were equivalent to concentrations in the soil solution ranging from 1.4 μM for p-hydroxybenzoic acid to <10 nM for ferulic acid (Whitehead et al 1981). Amounts up to 2000 times greater than these were extracted by 2 M NaOH. Kaminsky and Muller (1978) recommend against the use of alkaline soil extraction in the study of allelopathy, because the use of an alkaline extractant results in the chemical modification of the compound under study, and the compounds which are not solubilized by neutral extractants may not be available to plants. However, localized concentrations of phenolic acids close to fragments of decomposing plant material might be sufficiently high to have some effect. Moreover, Rice (1979)

considers that some compounds may influence plant growth at concentrations at which they are completely adsorbed by soil particles and are not extractable with water.

REFERENCES CITED

- Acharya, C. N. 1935a. Studies on the anaerobic decomposition of plant materials. I. The anaerobic decomposition of rice straw (Oryza sativa). Biochem. J. 29:528-541.
- Acharya, C. N. 1935b. Studies on the anaerobic decomposition of plant materials. II. Some factors influencing the anaerobic decomposition of rice straw. Biochem. J. 29:953-960.
- Acharya, C. N. 1935c. Studies on the anaerobic decomposition of plant materials. III. Comparison of the course of decomposition under anaerobic, aerobic, and partially aerobic conditins. Biochem. J. 29:1116-1120.
- Adamson, J. A., A. J. Francis, J. M. Duxbury, and M. Alexander. 1975. Formation of volatile organic products in soil under anaerobiosis. I. Metablism of glucose. Soil Biol. Biochem. 7:45-50.
- Agricultural Research Council Letcombe Laboratory. 1976. Annual report for 1975. Wantage, UK. pp. 29-31.
- Agricultural Research Council Letcombe Laboratory. 1977. Annual report for 1976. Wantage, UK. 107 p.
- Asami, T., and Y. Takai. 1963. Formation of methyl mercaptan in paddy soils (II). Soil Sci. Plant Nutr. 9:65-69.
- Banwart, W. L., and J. M. Bremner. 1974. Gas chromatographic identification of sulphur gases in soil atmospheres. Soil Biol. Biochem. 6:113-115.

- Banwart, W. L., and J. M. Bremner. 1975. Identification of sulfur gases evolved from animal manures. *J. Environ. Qual.* 4:363-366.
- Banwart, W. L., and J. M. Bremner. 1976a. Volatilization of sulfur from unamended and sulfate treated soils. *Soil Biol. Biochem.* 8:19-22.
- Banwart, W. L., and J. M. Bremner. 1976b. Evolution of volatile compounds from soils treated with sulfur containing organic materials. *Soil Biol. Biochem.* 8:439-443.
- Borner, H. 1955. Phenolic compounds from straw and stubble of wheat, barley, and rye (in German). *Naturwissenschaften* 42:583-584.
- Borner, H. 1956. Paperchromatographic identification of ferulic acid in the water extracts of straw and stubble of wheat, barley, and rye (in German). *Naturwissenschaften* 43:129-130.
- Chandrasekaran, S., and T. Yoshida. 1973. Effect of organic acid transformations in submerged soils on growth of the rice plant. *Soil Sci. Plant Nutr.* 19:39-45.
- Cho, D. Y., and F. N. Ponnampereuma. 1971. Influence of soil temperature on the chemical kinetics of flooded soils and the growth of rice. *Soil Sci.* 112:184-194.
- Chou, C. H., and H. J. Lin. 1976. Autointoxication mechanism of Oryza sativa. I. Phytotoxic effects of decomposing rice residues in soils. *J. Chem. Ecol.* 2:353-367.

- Doelle, H. W. 1975. Bacterial metabolism. Second edition. Academic Press, New York. 738 p.
- Gotoh, S., and Y. Onikura. 1971. Organic acids in flooded soil receiving added rice straw and their effect on the growth of rice. Soil Sci. Plant Nutr. 17:1-8.
- International Rice Research Institute. 1965. Annual report for 1964. Los Baños, Philippines. 357 p.
- Kaminsky, R., and W. H. Muller. 1978. A recommendation against the use of alkaline soil extractions in the study of allelopathy. Plant and Soil 49:641-645.
- Kamura, T., Y. Takai, and K. Ishikawa. 1963. Microbial reduction mechanisms of ferric iron in paddy soils (Part I). J. Sci. Soil Manure, Jpn. 32:135-138.
- Kubota, M., and C. Furusaka. 1981. Formation of 2,3-butane-diol, acetoin, ethanol, and butanol in paddy soils (in Japanese). J. Sci. Soil Manure, Jpn. 52:149-154.
- Kuwatsuka, S., and H. Shindo. 1973. Behavior of phenolic substances in the decaying process of plants. I. Identification and quantitative determination of phenolic acids in rice straw and its decayed product by gas chromatography. Soil Sci. Plant Nutr. 19:219-227.
- Lynch, J. M. 1978. Production and phytotoxicity of acetic acid in anaerobic soils containing plant residues. Soil Biol. Biochem. 10:131-135.

- Minami, K., K. Okayama, and S. Fukushi. 1981. Volatile sulfur compounds evolved from paddy soils treated with organic materials (in Japanese). *J. Sci. Soil Manure, Jpn.* 52:375-379.
- Okazaki, M., H. Wada, and Y. Takai. 1981. Reducing organic substances responsible for removal of Fe (III) and Mn (IV) from subsurface horizon of lowland rice soil. Pages 235-250 in Institute of Soil Science, Academic Sinica, ed. *Proceedings of Symposium on Paddy Soil*. Science Press, Beijing, China.
- Patrick, Z. A. 1971. Phytotoxic substances associated with the decomposition in soil of plant residues. *Soil Sci.* 111:13-18.
- Ponnamperuma, F. N. 1972. The chemistry of submerged soils. *Adv. Agron.* 24:29-96.
- Rao, D. N., and D. S. Mikkelsen. 1977. Effect of rice straw additions on production of organic acids in a flooded soil. *Plant Soil* 47:303-311.
- Rice, E. L. 1979. Allelopathy -- an update. *Botanical Review* 45:15-109.
- Shindo, H., and S. Kuwatsuka. 1975a. Behavior of phenolic substances in the decaying process of plants. I. Changes of phenolic substances in the decaying process of rice straw under various conditions. *Soil Sci. Plant Nutr.* 21:215-225.

- Shindo, H., and S. Kuwatsuka. 1975b. Behavior of phenolic substances in the decaying process of plants. III. Degradation pathway of phenolic acids. *Soil Sci. Plant Nutr.* 21:227-238.
- Shindo, H., and S. Kuwatsuka. 1976. Behavior of phenolic substances in the decaying process of plants. IV. Adsorption and movement of phenolic acids in soils. *Soil Sci. Plant Nutr.* 22:23-33.
- Shindo, H., and S. Kuwatsuka. 1977. Behavior of phenolic substances in the decaying process of plants. VI. Changes in quality and quantity of phenolic substances in the decaying process of rice straw in a soil. *Soil Sci. Plant Nutr.* 23:319-332.
- Shindo, H., and S. Kuwatsuka. 1978. Behavior of phenolic substances in the decaying process of plants. IX. Distribution of phenolic acids in soils of paddy fields and forests. *Soil Sci. Plant Nutr.* 24:233-243.
- Takai, Y. 1970. The mechanism of methane fermentation in flooded paddy soil. *Soil Sci. Plant Nutr.* 16:238-244.
- Takai, Y., and T. Asami. 1962. Formation of methyl mercaptan in paddy soils I. *Soil Sci. Plant Nutr.* 8:132-136.
- Takai, Y., T. Koyama, and T. Kamura. 1957. Microbial metabolism of paddy soils. Part III. Effect of iron and organic matter on the reduction process (1). *J. Agr. Chem. Soc. Jpn.* 31:211-215.

- Takaishi, S., K. Tasaki, and M. Imai. 1909. Formation of organic acids during the decomposition of organic manures (part I, in Japanese). Nougaku-kai-hou 89:3-8.
- Takeda, K., and C. Furusaka. 1970. Studies on the bacteria isolated anaerobically from paddy field soil. Rep. Ins. Agric. Res. Tohoku Univ. 21:1-22.
- Takeda, K., and C. Furusaka. 1975a. Studies on the bacteria isolated anaerobically from paddy field soil. III. Production of fatty acids and ammonia by *Clostridium* species. Soil Sci. Plant Nutr. 21:119-127.
- Takeda, K., and C. Furusaka. 1975b. Studies on the bacteria isolated anaerobically from paddy field soil. IV. Model experiments on the production of branched fatty acids. Soil Sci. Plant Nutr. 21:119-127.
- Takijima, Y. 1960. Metabolism of organic acids in soils and their harmful effects on paddy rice growth (part I). Column chromatography of organic acids using home-made silica gel and its application to soil samples (in Japanese). J. Sci. Soil Manure, Jpn. 31:435-440.
- Takijima, Y. 1963. Studies on behavior of the growth inhibiting substances in paddy soils with special reference to the occurrence of root damage in the peaty paddy fields (in Japanese, English summary). Bulletin of the National Institute of Agricultural Sciences (Japan) Series B. 13:117-252.

- Takijima, Y. 1964. Studies on organic acids in paddy field soils with reference to their inhibitory effects on the growth of rice plants: 2. Soil Sci. Plant Nutr. 10:212-219.
- Takijima, Y., M. Shiojima, and Y. Arita. 1960. Metabolism of organic acids in soils and their harmful effects on paddy rice growth (part 2). Effect of organic acids on root elongation and nutrient absorption of rice plants (in Japanese). J. Sci. Soil Manure, Jpn. 31:441-446.
- Tsutsuki, K., and S. Kuwatsuka. 1978. Chemical studies on soil humic acids. II. Composition of oxygen containing functional groups of humic acids. Soil Sci. Plant Nutr. 24:547-560.
- Walters, E. H. 1917. The isolation of p-hydroxybenzoic acid from soil. Am. Chem. Soc. J. 39:1178-1784.
- Wang, T. S. C., T. K. Yang, and T. T. Chuan. 1967a. Soil alcohols, their dynamics and their effect upon plant growth. Soil Sci. 104:40-45.
- Wang, T. S. C., T. Yang, and T. Chung. 1967b. Soil phenolic acids as plant growth inhibitors. Soil Sci. 103:239-246.
- Watanabe, I., and C. Furusaka. 1980. Microbial ecology of flooded rice soils. Pages 125-168 in M. Alexander, ed. Advances in Microbial Ecology, Vol. 4.

- Whitehead, D. C. 1964. Identification of p-hydroxybenzoic vanillic, p-coumaric and ferulic acids in soils. *Nature*, London 202:417-418.
- Whitehead, D. C., H. Dibb, and R. D. Hartley. 1981. Extractant pH and the release of phenolic compounds from soils, plant roots and leaf litter. *Soil Biol. Biochem.* 13:343-348.
- Winter, A. G. 1955. Occurrence and significance of antimicrobial and antiphytotoxic substances in natural soils (in German). *Zeits. Pflanzenernah, Dung, Bodenk.* 69:224-233.
- Yamane, I., and K. Sato. 1967. Effect of temperature on the decomposition of organic substances in flooded soil. *Soil Sci. Plant Nutr.* 13:94-100.
- Yamane, I., and K. Sato. 1970. Plant and soil in a lowland rice field added with forage residues. *Rep. Inst. Agr. Res. Taihoku Univ.* 21:79-101.

Table 1. Characteristics of soil samples.

Soil type	pH	C	Total N (%)	Active Fe
Pila clay loam	7.2	2.48	0.204	0.32
Maahas clay	6.0	1.43	0.140	1.39
Luisiana clay	5.4	1.56	0.117	1.89

Table 2. Analyses of organic materials.

Material	C	Total N (%)	C/N
Rice straw	39.6	0.56	70.5
Rice straw compost	14.2	1.69	8.4
Green manure	45.8	3.21	14.3

Table 3. Sulfur containing gases evolved from a submerged soil (Nyuzen) treated with organic materials (adapted from Minami et al 1981).

Compound	Amount (nmol/kg soil)			
	Control	Rice straw	Compost	Cystine
H ₂ S	0	1700	0	4720
COS	17	78	23	566
CS ₂	7	4	8	71
CH ₃ SH	17	56	0	145
CH ₃ SCH ₃	129	483	129	113
CH ₃ SSCH ₃	53	54	0	74

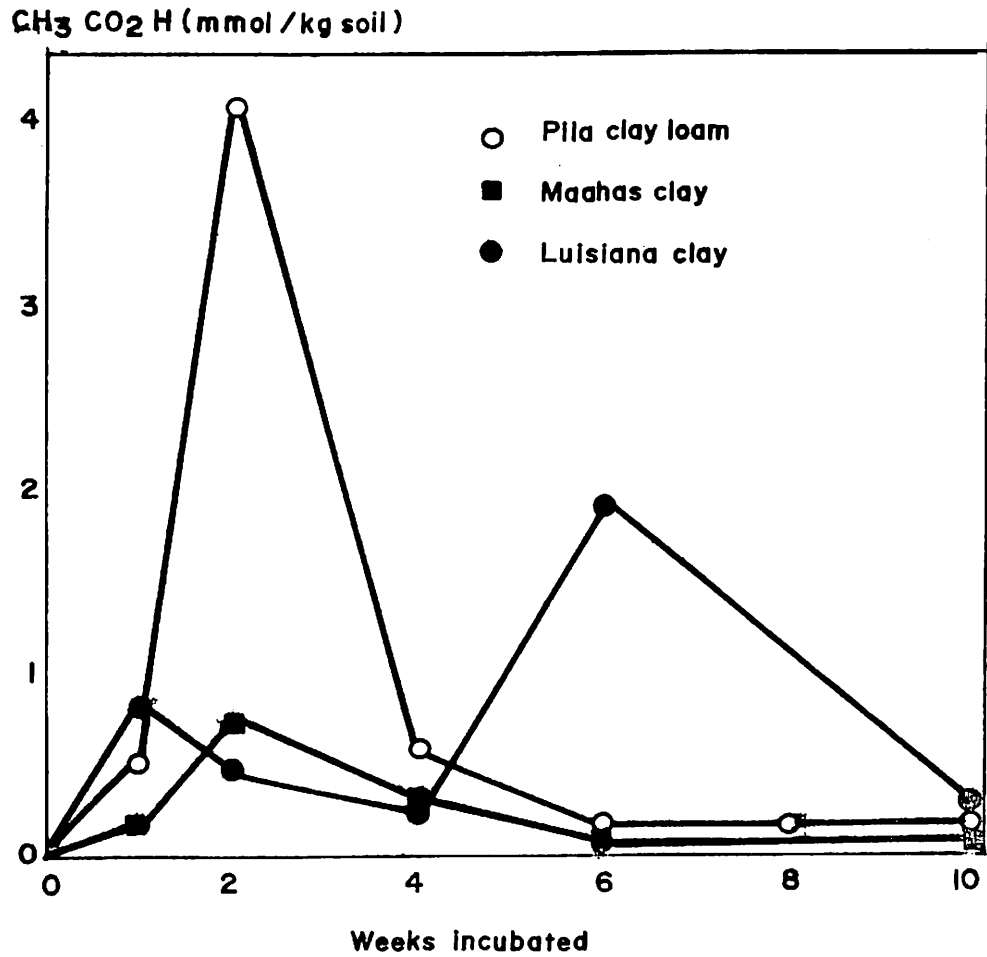


Fig. 1. Kinetics of acetic acid in 3 submerged soils treated with rice straw (0.25%) at 20°C.

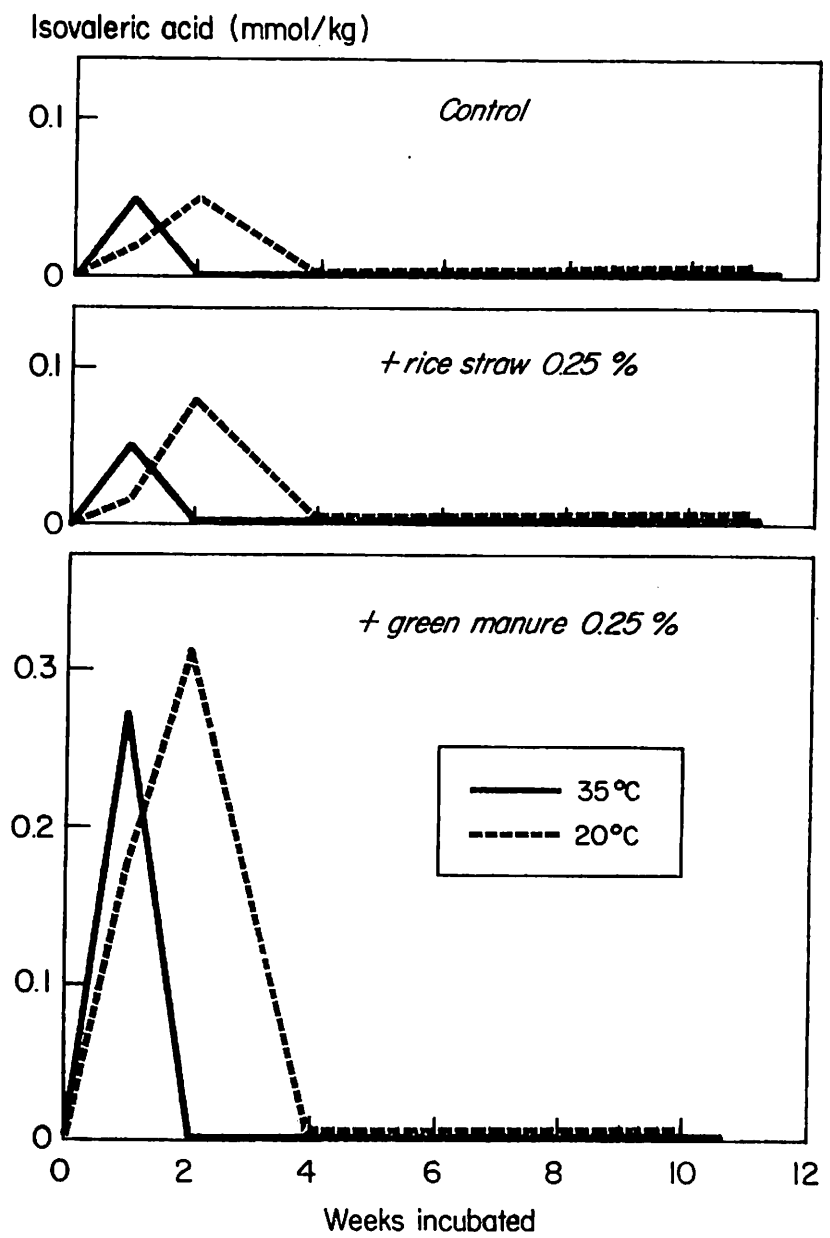
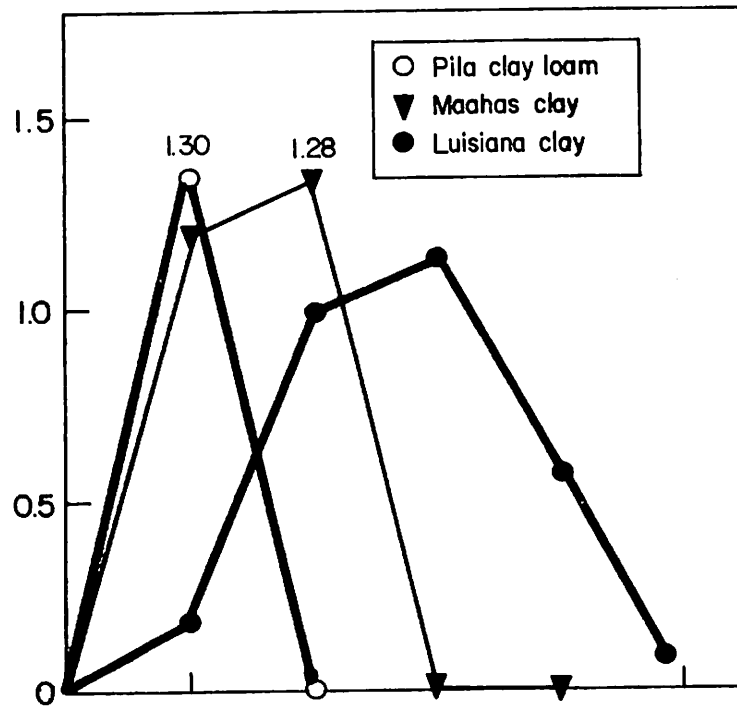


Fig. 2. Effect of organic matter on kinetics of isovaleric acid in submerged Pila clay loam at 20 and 35°C.

Methanol (mmol/kg)



Ethanol (mmol/kg)

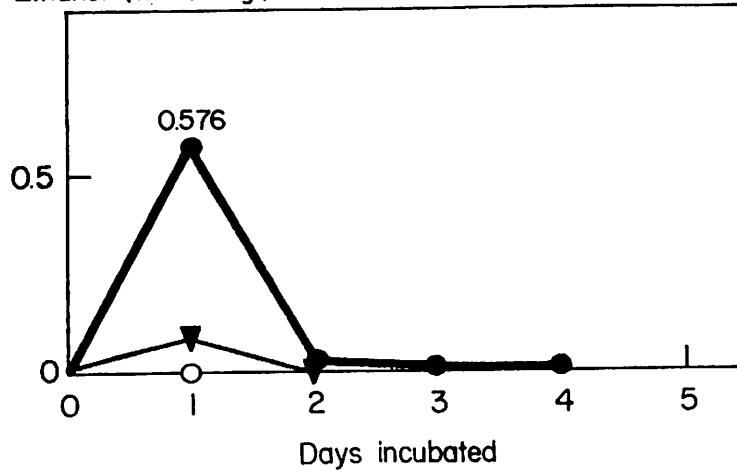


Fig. 3. Kinetics of alcohols in 3 submerged soils treated with green manure (1%) at 35°C.

Phenolic acid (μ mol/kg)

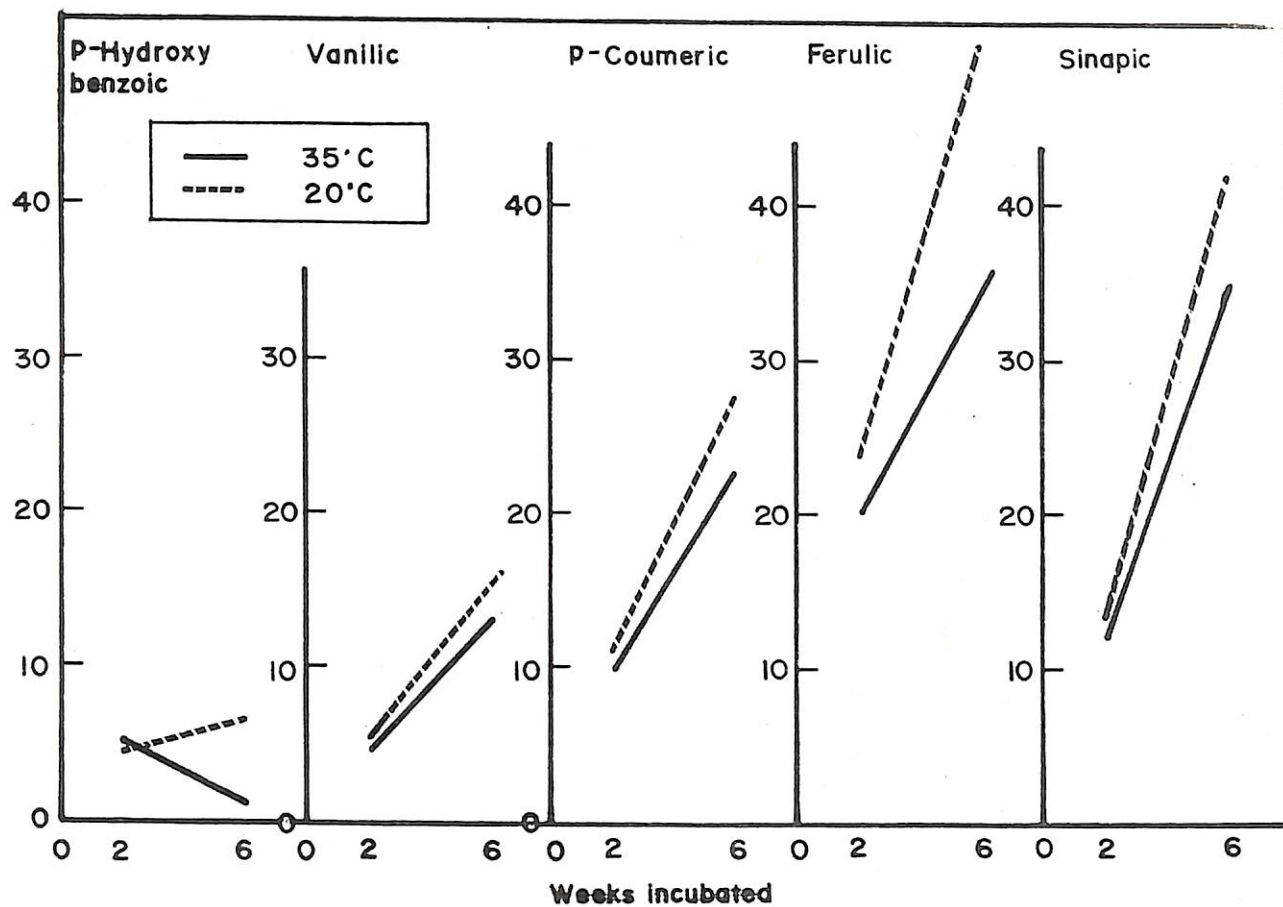


Fig. 4. Kinetics of phenolic acids in submerged Louisiana clay treated with rice straw (0.25%).