

22P

Humic Substances in Straw Compost with Rock Phosphate

C. P. Singh* & A. Amberger

Institute of Plant Nutrition, Technical University Munich,
8050 Freising-Weihenstephan, FRG

(Received 20 May 1989; revised version received 24 May 1989;
accepted 6 June 1989)

ABSTRACT

The production of humic substances and their retention capacities for phosphorus and calcium released during composting of wheat straw with two types of low-grade rock phosphate were examined. Relative quantities of humic acids increased with increase of composting time, while fulvic acids production decreased after 30 days of composting. The addition of both Mussoorie and Hyperphos retarded humic acids production and enhanced fulvic acids production. Molasses incorporation had no effect on humic acids but increased fulvic acids production. The production of humic acids and their retention capacity for P and Ca were greater in the presence of Mussoorie phosphate than in the presence of Hyperphos, but fulvic acids formation was higher with Hyperphos. About 80-85% P and 90-95% Ca retained by the total humic substances were found in the fulvic acids fraction.

INTRODUCTION

The composting of low grade rock phosphate with agricultural wastes is known to increase the solubility of insoluble phosphates (Singh *et al.*, 1983, 1987; Kubát *et al.*, 1985; Singh, 1985; Mey *et al.*, 1986). Although the extent of solubilisation can vary with the kind of waste, the rate of organic matter decomposition during composting is of primary importance. Most researchers have assumed that organic acids produced during organic

* Present address: Department of Soils, Haryana Agricultural University, HISAR-125004, India.

matter decomposition are mainly responsible for the mobilisation of insoluble phosphates. They have also postulated that humic substances, a resultant of organic matter decomposition, may supply some organic functional groups or anions that can effectively chelate Ca^{2+} ions and create a driving force for further dissolution of rock phosphate (Drake, 1964; Chien, 1979). Villarreal & Augstburger (1984) showed the beneficial effect of farm-yard manures on increasing phosphorus availability from rock phosphate dissolution. The mechanism of solubilisation was explained on the basis of studies made on soil organic matter decomposition. There is no single report available of a compost system where the effects would be more pronounced than in the soil system. Therefore, a study on the production of humic substances during the preparation of rock phosphate-enriched compost is needed in order to understand the role of humic substances with regard to rock phosphate solubilisation.

The purpose of this study was to quantify the production of humic substances and to see their retention capacity of Ca and P released from rock phosphate during the preparation of wheat-straw compost.

METHODS

Wheat straw was collected from the institute farm and ground to pass through a 1-mm sieve. The chemical composition is given in Table 1. There were five treatment combinations containing wheat straw, Mussoorie phosphate (M. phos), Hyperphos and molasses as shown in Table 2. Both rock phosphates are from sedimentary rock and come in the soft grade. Mussoorie phosphate contains a lower percentage of total P_2O_5 than Hyperphos, but the presence of organic carbon in significant amounts shows the loose configuration of the apatite structure. The value for 2% formic acid-soluble P_2O_5 in M. phos is very low due to its high free- CaCO_3 content.

Four grams of wheat straw were weighed into 50-ml polyethylene bottles and both rock phosphates were added separately at the rate of 1 g per 4 g wheat straw on a freeze-dried straw basis. This ratio had given maximum solubilisation in the earlier experiment (Singh, 1985). Molasses at the rate of 0.5 g in each case was added to enhance the microbial activity during composting (Alexander, 1977). The C:N ratio of the mixture was adjusted to 30 in all the treatments by adding cattle urine for the quick decomposition. The mixture was then inoculated with 1 ml aqueous extract of a natural inoculant containing 5% each of soil, dung and old compost. Finally, moisture was maintained at 200% of freeze-dried weight of the mixture. After thorough mixing, eight bottles for each treatment were incubated, loosely stoppered, at 30°C.

TABLE 1
Some Chemical Characteristics of the Raw Materials Used in Composting

Characteristics (%)	Methods	Wheat straw	Molasses ^a	Cattle ^a urine	Inoculant ^a extract	Mussoorie phos	Hyperphos
Organic carbon	Springer & Klee, 1955	42.150	24.820	0.780	0.050	1.610	0.270
Nitrogen	Kjeldahl, 1951	0.511	1.905	0.503	0.002	—	—
Total P_2O_5	by Micro-vanadate	0.061	0.016	0.002	0.001	19.510	30.480
Formic acid-soluble P_2O_5 (% of total P_2O_5)	Hoffmann & Mager, 1953	—	—	—	—	7.073	67.510
Total Ca	by Flamephotometer	0.580	0.082	0.003	0.012	22.800	37.000
CaCO_3	Scheibler, 1954	—	—	—	—	20.300	16.700

^a On liquid basis.

— Not determined.

TABLE 2
Per Cent Loss of Organic Matter during Preparation of Rock Phosphate-Enriched Compost

Treatment	Composting period (days)		
	30	60	120
Wheat straw (alone)	13.3	22.7	26.7
+ Mussooric phos	20.6	31.5	41.7
+ Mussooric phos + molasses	24.2	34.9	47.8
+ Hyperphos	17.6	26.9	37.1
+ Hyperphos + molasses	21.7	31.7	44.2

LSD at 5%: treats 1.35; days 1.05; treats × days 2.34

The contents of the bottles were mixed after 7, 20, 30, 60 and 90 days of incubation and distilled water was added to return the moisture to the original level. Duplicate bottles for each treatment were removed at 0, 30, 60 and 120 days of incubation. After freeze-drying, humic and fulvic acids were extracted with 0.1 N NaOH by using the method of Schlichting and Blume (1966). The relative percentages of humic and fulvic acids in the total organic matter were calculated by determining the organic matter by a wet oxidation technique (Springer & Klee, 1955). Inorganic P and Ca were determined in humic and fulvic acids after clarifying them, by the method of John (1970) for P and by flamephotometer for Ca. Total P and Ca were estimated after the digestion of humic and fulvic acids with perchloric and sulphuric acids. The retentions of P and Ca by humic and fulvic acids were calculated by subtracting their inorganic forms from the total contents.

RESULTS AND DISCUSSION

The rate of mineralisation of organic matter during composting was measured by determining the loss of organic matter (Table 2). The amount of mineralisation increased significantly with incubation time in all the treatments. Mineralisation was very slow in the wheat straw alone, but it was increased considerably on the addition of both M. phos and Hyperphos. This shows that phosphorus was the limiting factor for the microbial growth in the wheat straw, which contained a very small amount of phosphorus (Table 1). Molasses incorporation further improved the extent of mineralisation over rock phosphate addition alone. This might be due to the higher availability of water-soluble carbohydrates to the microbial population (Alexander, 1977). Mey *et al.* (1986) also showed that the addition of sucrose

TABLE 3
Relative Percentage of Humic Substances Produced during Preparation of Rock Phosphate-Enriched Compost

Treatment	Composting period (days)			
	0	30	60	120
Wheat straw (alone)				
+ Mussooric phos	2.5	8.3	14.6	15.5
+ Mussooric phos + molasses	2.4	7.6	10.2	13.8
+ Hyperphos	2.7	7.6	10.1	13.5
+ Hyperphos + molasses	2.2	6.0	7.7	11.6
+ Hyperphos	2.7	6.8	8.3	11.4

LSD at 5%: treats 0.36; days 0.32; treats × days 0.72

Fulvic acids (% of organic matter)

Wheat straw (alone)	4.1	19.3	13.6	9.0
+ Mussooric phos	4.3	21.7	15.8	11.6
+ Mussooric phos + molasses	4.1	26.8	20.5	13.6
+ Hyperphos	4.5	23.5	17.2	12.9
+ Hyperphos + molasses	4.6	27.8	21.7	14.4

LSD at 5%: treats 0.42; days 0.37; treats × days 0.83

to a cellulose mixture increased the rate of organic matter mineralisation. At all time intervals, M. phos gave significantly higher loss of organic matter than Hyperphos, most probably due to its higher CaCO₃ content increasing microbial growth during composting.

The data on the relative percentages of humic and fulvic acids in the total organic matter (Table 3) show that the production of humic acids increased with time while fulvic acids increased up to 30 days and then decreased continuously in all the treatments. This suggested that during composting of wheat straw fulvic acids are produced initially in high quantities and then they are converted gradually into humic acids with the maturation of the compost. According to Konomova (1961) humic and fulvic acids are linked by a sequence of a single inter-convertible chain. Both rock phosphates, with or without molasses, retarded humic acids formation and enhanced the formation of fulvic acids. In the presence of M. phos the production of humic acids was higher than in the presence of Hyperphos. This trend was reversed in the case of fulvic acids. A slow rate of mineralisation might favour the formation of fulvic acids during composting of wheat straw. The maximum conversion of organic matter into humic plus fulvic acids was 27–35% at 30 days of composting and then decreased gradually, reducing to

TABLE 4
Retention of Phosphorus (μg) by Humic Substances Produced from 1 g Straw during Composting

Treatment	Composting period (days)			
	0	30	60	120
	<i>By humic acids</i>			
Wheat straw (alone)	7	16	20	25
+ Mussooric phos	6	42	109	242
+ Mussooric phos + molasses	5	66	144	286
+ Hyperphos	6	25	60	177
+ Hyperphos + molasses	5	41	73	208

LSD at 5%: treats 1.76; days 1.58; treats \times days 3.53

between 24 and 27% at 120 days in different treatments. The humification (humic + fulvic acid production) was highest up to 30 days and thereafter mineralisation predominated over humification.

The retention of phosphorus increased as the humic acids increased with composting time (Table 4). Humic acids produced in the presence of both rock phosphates and molasses retained a significantly higher amount of phosphorus than the humic acids produced during the composting of wheat straw alone, although the production of humic acids was lower in the presence of rock phosphate. This indicates that humic acids produced from the composting of wheat straw alone had the capacity to retain phosphorus but showed a lower retention due to the unavailability of phosphorus. About 80-85% of the total phosphorus content of the humic substances was held in the fulvic acids fraction. This bulk of P_0 in fulvic acids could not be an integral part of the molecules. A large part of it might be linked through cationic bonds. Dormaar (1972) and Fares *et al.* (1974) explained the formation of a $\text{P}\text{---}\text{Ca}\text{---}$ humate complex in an organic soil system. Bowman & Cole (1978) reported that about 50% of soil fulvic acids P was found in an organic combination and the rest was adsorbed or fixed through cationic bonds.

TABLE 5
Retention of Calcium (μg) by Humic Substances Produced from 1 g Straw during Composting

Treatment	Composting period (days)			
	0	30	60	120
	<i>By fulvic acids</i>			
Wheat straw (alone)	73	130	195	253
+ Mussooric phos	57	171	272	376
+ Mussooric phos + molasses	70	175	347	430
+ Hyperphos	38	149	210	291
+ Hyperphos + molasses	44	159	281	368

LSD at 5%: treats 1.78; days 1.60; treats \times days 3.57

Treatment	Composting period (days)			
	0	30	60	120
	<i>By fulvic acids</i>			
Wheat straw (alone)	1029	1215	820	779
+ Mussooric phos	1009	5320	2963	1824
+ Mussooric phos + molasses	1020	6693	3129	2276
+ Hyperphos	1064	5442	2997	1390
+ Hyperphos + molasses	1074	6713	3159	1674

LSD at 5%: treats 8.0; days 7.2; treats \times days 16.0

A similar trend was observed with Ca retention (Table 5) as with phosphorus, but a very high amount of Ca was held in the fulvic acids fraction. This very high retention of Ca by fulvic acids was possibly due to two reasons. Firstly, fulvic acids were produced in higher quantities and secondly, their reactivity was higher because they contain greater amounts of ---COOH and alcoholic ---OH groups per unit weight than do humic acids. Schmitzer (1982) reported that the acidity or exchange-capacity of humic substances is due mainly to the occurrence of ionisable H ions of ---COOH and ---OH groups found in aliphatic chains or aromatic rings of the molecules.

The per cent retention of P and Ca was calculated by summation of the average values for humic and fulvic acids for different treatments (Table 6). The retention of P and Ca by humic substances in the presence of M. phos increased by 160 and 167% respectively over the retention by humic substances produced during composting of wheat straw alone. Molasses addition further improved the retention, reaching 213% for P and 215% for Ca. These values are equivalent to 4.0 and 7.9% of the total P and Ca of the compost, respectively. In the case of Hyperphos the per cent increase was slightly lower than with M. phos, but the values for % total P and % total Ca

TABLE 6
Per Cent Retention of P and Ca in Humic Substances (Humic + Fulvic Acids) Produced from 1 g Straw during Composting

Treatment	Average P ($\mu\text{g/g}$)	Increase over control (%)	Per cent of total P	Average Ca ($\mu\text{g/g}$)	Increase over control (%)	Per cent of total Ca
Wheat straw (control)	198	—	32.6	1 124	—	23.7
+ Mussoorie phos	515	160	3.0	2 998	167	6.3
+ Mussoorie + molasses	620	213	4.0	3 535	215	7.9
+ Hyperphos	500	152	1.9	2 895	158	3.8
+ Hyperphos + molasses	590	197	2.3	3 368	200	4.9

are very low because Hyperphos contains a larger amount of both total P and Ca and was added equal to M. phos on a weight basis.

The results obtained in this study suggest that the incorporation of rock phosphate with or without molasses to the composting material may shorten the time of composting by increasing the rate of mineralisation, and at the same time the quality of the compost will also be improved due to increased humic substances. Humic substances, especially fulvic acids, adsorb a significant amount of Ca and release H^+ ions which help in rock phosphate solubilisation. Humic substances produced during composting may also check the reprecipitation of solubilised P and Ca by complexing both ions and creating a sink in the system for further dissolution of rock phosphate. Mussoorie phosphate had a slightly higher effect on total production of humic plus fulvic acids than did Hyperphos during the preparation of wheat straw compost.

ACKNOWLEDGEMENT

The senior author wishes to thank Alexander von Humboldt Stiftung, Jean Paul Str. 12, Bonn 2, FRG for providing a Post-doctoral fellowship during this investigation.

REFERENCES

- Alexander, M. (1977). *Introduction to Soil Microbiology*, 2nd edn. Wiley Eastern, New Delhi, India, pp. 241, 345.
- Bowman, R. A. & Cole, C. V. (1978). An exploratory method for fractionating of organic P from grassland soils. *Soil Science*, **125**, 95-101.
- Chien, S. H. (1979). Dissolution of phosphate rock in acid soils as influenced by nitrogen and potassium fertilizers. *Soil Science*, **127**, 371-6.
- Drake, M. (1964). In *Chemistry of the Soils*, ed. F. E. Bear. Van Nostrand-Reinhold, Princeton, New Jersey, pp. 395-444.
- Dornaar, J. F. (1972). Seasonal patterns of soil organic phosphorus. *Canadian Journal of Soil Science*, **52**, 107-12.
- Fares, F., Fardau, J. C. & Jacquin, F. (1974). Quantitative survey of organic phosphorus in different soil types. *Phosphorus in Agriculture*, **63**, ISMA.
- Hoffman, E. & Mager, D. (1953). Solubility of phosphoric acid and phosphate rocks. *Zeitschrift für Pflanzenernährung Düngung und Bodenkunde*, **62**, 262-4.
- John, M. K. (1970). Colorimetric determination of phosphorus in soil and plant material with ascorbic acid. *Soil Science*, **109**, 214-20.
- Kjeldahl, J. (1951). In *Methodenbuch Band III*, ed. R. Herrmann. Neumann, Radebeul, Berlin, pp. 18-20.
- Kononova, M. M. (1961). *Soil Organic Matter*. Pergamon Press, Oxford, London, pp. 97-8.

- Kubát, J., Novák, B. Pirk, J. & Macháček, V. (1985). Rock phosphate solubilisation in cattle slurry. *Zentralblatt für Microbiologie*, **140**, 449-54.
- Mey, P., Sayag, D. & André, L. (1986). Chemical or microbiological solubilisation of rock phosphate. *Comptes Rendus des Séances de L'Académie d'Agriculture de France*, **72**, 81-9.
- Schreiber, C. (1954). In *Methodenbuch II*, ed. R. Hartmann. Neumann, Radebeul, Berlin, pp. 65-8.
- Schliching, E. & Blume, H. P. (1966). *Bodenkundliches Praktikum*. Paul Parey, Hamburg, Berlin, pp. 136-8.
- Schnitzer, M. (1982). In *Methods of Soil Analysis, Part 2*, 2nd edn, ed. A. L. Page. ASA-SSSA, Segal Rd, Madison, WI 53711, USA, p. 587.
- Singh, C. P. (1985). Preparation of phospho-compost and its effect on the yield of Moong bean and wheat. *Biological Agriculture and Horticulture*, **2**, 223-9.
- Singh, C. P., Ruhai, D. S. & Mahendra Singh (1983). Solubilisation of low grade rock phosphate by composting with a farm waste, Pearl-Millet Boobhi. *Agricultural Hastes*, **8**, 17-25.
- Singh, C. P., Ruhai, D. S. & Singh, M. (1987). The solubilisation of low grade rock phosphate with anaerobic digester slurry. *International Biodeterioration*, **23**, 249-56.
- Springer, V. & Klec, J. (1955). Feststellung der optimalen Reaktionsverhältnisse beim reduktrometrischen Chromschwefelstureverfahren zur Schnellbestimmung von Kohlenstoff und Vorschlag einer verbesserten Arbeitsweise. *Zeitschrift für Pflanzenernährung, Düngung und Bodenkunde*, **71**, 193-208.
- Villarroel, J. & Augstburger, F. (1984). In *La Roca Fosforica*, Vol. 2, ed. V. Ricaldi & S. Escalera. GLIRF, Cochabamba, Bolivia.