

AN ABSTRACT OF THE THESIS OF

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Title: Transformations of Sulfur in Wetland Rice Soils

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Richard P. Dick

In recent years sulfur (S) deficiency has emerged as constraint to rice production in many tropical areas of the world. However, there is relatively little information on S transformations under the typical rice growing conditions--flooded--and rainfed flooding and drying cycles. This information is necessary for efficient S cycling and crop fertilization and to minimize input costs.

Incubation studies were undertaken with the objective of determining the effect of organic residues: 1) on rates of mineralization of S and N, and P release, in soils under continuous flooding; 2) with varying C:S ratios on rates of mineralization of S and N, and P release in soils under aerobic-flooding cycles; and 3) on the transformations of organic S fractions in wetland rice soil under continuous flooding or aerobic-flooding cycles.

Incubation studies involving objectives 1 and 2 were carried out using soil incubation leaching columns, where incubated soils were leached periodically with deionized water to remove and measure the released S, N, or P. To study objective 3, static incubation systems were used where soils were destructively sampled and analyzed for S fractions and other chemical properties.

The organic residues (25 mg g⁻¹ soil) used in the incubation studies included: rice straw (*Oryza sativa* L.), pea vine (*Pisum sativum* L.), or wheat straw (*Triticum aestivum* L.) with C:S ratio of 100:1 or 400:1. The moisture treatments were: continuous flooding or aerobic (75% of field capacity) - flooding cycles with

two or four weeks aerobic-flooding cycles.

The potentially mineralizable S pool (S_0) and first-order rate constant (K_S) values varied among the soils and types of added organic residues. Sulfur mineralization under flooded condition amended with organic residues depends on soil type, nature of organic residues and incubation period.

The potentially mineralizable N pool (N_0) in soils amended with rice straw or pea vine in flooded condition was several times greater than the unamended soils. The K_N values for rice straw treated soils were 1.5 to 3.5 times more than unamended soils. High rates of N mineralization in the rice straw treatment was due to a lower C:N ratio (14:1) than wider ratio (30:1) of pea vine.

Soils treated with rice straw under flooded condition showed a significantly higher cumulative PO_4 release over control or pea vine treatment. Low PO_4 released in pea vine treatment was due to immobilization of P because of wide C:P ratio (252:1) of pea vine.

Soils treated with wheat straw with a C:S ratio of 100:1 produced significantly higher cumulative SO_4 -S than straw with a ratio of 400:1 or in the control at two or four weeks aerobic-flooding cycles, indicating more mineralization of S. The S_0 values were twice as much with a C:S ratio of 100:1 as with straw with a 400:1 ratio.

Under aerobic-flooding cycles the N_0 values in straw treated soils were 2 to 5.7 times more than the control treatment. K_N values in straw treatments were lower than the control, indicating low microbial degradation of organic N.

Cumulative amount of PO_4 -P released in soils amended with organic residues under aerobic-flooding cycles was linearly related with time of incubation.

Distribution of S fraction (% of total S) showed a considerable increase in ester SO_4 -S and reduced-S with a decrease in C-bonded S and SO_4 -S under continuous flooding conditions. Conversely, SO_4 -S and residual S fraction were significantly increased in aerobic-flooding cycles. Aerobic-flooding cycle provided 4 to 8 times more plant available SO_4 -S than under continuous flooding.

TRANSFORMATIONS OF SULFUR IN WETLAND RICE SOILS

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M. Mujibul Islam

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APPROVED:

Redacted for Privacy

Associate Professor of Crop and Soil Science in charge of major

Redacted for Privacy

Head of Department of Crop and Soil Science

Redacted for Privacy

Dean of Graduate School

Date thesis is presented June 26, 1992

Typed by Pam Wegner for M. Mujibul Islam

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TRANSFORMATIONS OF SULFUR IN WETLAND RICE SOILS

INTRODUCTION

Sulfur (S) is an essential element for both plants and animals. It is a constituent of proteins and other biological compounds which are involved in many metabolic processes. Plants require S for the synthesis of essential amino acids and proteins, certain vitamins and co-enzymes, glucoside oils, structurally and physiologically important disulfide linkages and sulfhydryl groups, and activation of certain enzymes (Coleman, 1966).

In recent years S deficiency has been recognized as a major constraint to agricultural systems in many tropical areas of the world (IFDC, 1979). Morris (1987) reported S deficiencies in 73 countries of the world including Asia, Europe, Africa, Americas, and Oceania. Response to S has been reported by Blair et al. (1980) in 23 crops in 40 tropical countries. Morris (1987) attributed the reasons for the increasing incidence of S deficiencies primarily to: increased use of high analysis fertilizers containing little or no S, multiple cropping, higher yielding crops, greater control of industrial emission of S, decreased use of S in pesticides, declining reserves of soil S, and use of crop residues for feed and fuel.

Sulfur in agricultural soils occurs in organic and inorganic forms, with organic S accounting for more than 95% of the total S (Tabatabai, 1984). The proportion of organic and inorganic S in soils, however, varies widely according to soil type and depth of sampling. Three broad fractions of organic S in soils are: hydriodic (HI) acid

reducible S (primarily ester sulfates), C-bonded S (mainly amino acids), and unidentified S (residual or inert). Analyses of a wide range of soils show that from 25 to 75% of the organic S in soils is HI reducible, from 7 to 30% in C-bonded S and from 11 to 22% is unidentified S (Tabatabai, 1984). In tropical surface soils Tabatabai and Bremner (1972a) found a significant correlation of total S, organic S and ester SO_4 with organic C and total N content of the soils.

In the soil, organic S contents are highly correlated with organic carbon (C) and nitrogen (N). The relative proportion of C:N:Organic S is approximately 140:10:-1.3 and does not vary greatly on a world-wide basis (Probert and Samosir, 1983). Very little information is available on the total S content and fractions of organic S in the rice soils of Bangladesh and their relationships with organic C, total N, and total and organic P content of the soils.

Submergence of a soil creates unique chemical and biological conditions which markedly affect S transformations. When a soil is submerged oxygen supply is drastically reduced and soil becomes anaerobic. Conversely, when oxygen supply from the atmosphere and from photosynthesis by algae and aquatic weeds exceeds oxygen consumption by soil microorganisms an oxidized zone is developed in the upper part of the flooded horizon of soils. In flooded soils planted to rice, another oxidized zone develops in the rhizosphere, in addition to the oxidized surface layer. There is no sharp dividing line between the oxidized and reduced zones in flooded soils. The S transformations which occur in flooded soils are largely biological and the main reactions are mineralization, immobilization, reduction of SO_4 , production of volatile S compounds and oxidation of elemental S and inorganic S compounds

(Freney and Boonjawat, 1983). Little information is available on the S mineralization/immobilization and transformations among organic S pools in flooded soils.

It is generally accepted that S is taken up by plant roots as SO_4 , which is produced by mineralization of soil organic S (Williams, 1975). Sulfatase enzymes hydrolyze organic SO_4 esters and play an important role in the processes by which soil organic S is mineralized and made available for plant growth (Freney, 1967).

Tabatabai and Bremner (1970b) reported that the arylsulfatase activity in temperate soils was correlated with organic C and the activity decreases with depth in the soil profile. Little information is available on S mineralization in relation to sulfatase activity in flooded soils.

In the tropics highly weathered soils containing Fe and Al oxides and kaolinitic clay can adsorb large amounts of SO_4 with decreases in sorption with increasing soil pH and P level (Kamprath and Till, 1983; Fox et al., 1971). In cultivated soils SO_4 adsorption is primarily in the B horizon, especially in soils that have been limed or treated with P and S fertilizers. The major difference between tropical and temperate soils lies in the adsorbed:soluble SO_4 ratio. Weathered tropical soils have higher pH dependent charge and higher anion exchange capacity (AEC) than temperate soils, and hence a greater capacity to adsorb anions such as SO_4 (Blair and Lefroy, 1987). The adsorbed SO_4 in the tropical soils can be an important source of plant available S providing it can desorb.

There is increasing attention by investigators on the role of biologically mediated processes in relation to the dynamics of nutrient transformations in soils. Microbial biomass S is an important fraction of the soil organic S. Although the

microbial mass contains only a small proportion of soil S, this fraction is extremely labile and is thought to be the key to understanding S turnover in soil (Biederback, 1978). Saggar et al. (1981) found that microbial biomass S in soil was approximately 2.5% of the total soil S. Currently no information is available on the microbial biomass S in wetland rice soils.

The objectives of this study were:

1. To observe the effect of organic residues on rates of mineralization of S and N, and P release, in soils under continuous flooding.
2. To measure the effect of organic residues with varying C:S ratios on rates of mineralization of S and N, and P release, in soils under aerobic-flooding cycles.
3. To observe the effect of added organic residues on the transformations of organic S fractions in wetland rice soil under continuous flooding or aerobic-flooding cycles.

LITERATURE REVIEW

Occurrence of Sulfur Deficiency in Crop Production

In recent years, S deficiency is recognized as a major constraint to agriculture systems in many tropical areas of the world (IFDC, 1979). Deficiencies of S have been reported with increasing frequency throughout the world in the past 20 years, and especially within the past 10 years with more frequent occurrences in the tropical regions. Morris (1987) reported S deficiencies in 73 countries of the world including

Asia, Europe, Africa, Americas, and Oceania. Response to S has been reported by Blair et al. (1980) in 23 crops in 40 tropical countries.

The reasons for the increasing incidence of S deficiencies can be attributed primarily to (Morris, 1987):

1. Increased use of high analysis fertilizers containing little or no S.
2. Multiple cropping and higher yielding crops which remove greater amounts of S from the soil.
3. Greater control of industrial emissions of S combined with the decreased use of high S fuels.
4. Decreased use of S in pesticides.
5. Declining reserves of soil S.
6. Use of crop residues for feed and fuel.

Contents and Forms of Sulfur in Soil

The total S amounts in surface horizons of tropical soil are generally low compared to temperate soils, averaging less than 250 mg S kg⁻¹ soil compared to temperate mollisols that can have >500 mg S kg⁻¹ soil (Blair, 1979). Under cultivation, long-term studies have shown a decline in the organic S levels of 50% in 20-30 years (Kamprath and Till, 1983). There are relatively few data available on the S status of soils in tropical Asia. Average values of total S for Malaysian soils was 213 mg S kg⁻¹ (Nor, 1981), 101 mg S kg⁻¹ soil for Indonesian soils (Ismunadji and Zulkarnaini, 1977), 165 mg S kg⁻¹ soil for Thailand soils (Chaiwanakupt et al., 1987),

445 mg S kg⁻¹ soil for rice soils of The Philippines (Islam and Ponnamperna, 1982) and 182 mg S kg⁻¹ soil for rice soils of India (Venkateswarlu et al., 1969).

Sulfur in agricultural soils occurs in organic and inorganic forms, with organic S accounting for more than 95% of the total S (Tabatabai, 1984). The proportion of organic and inorganic S in soils, however, varies widely according to soil type and depth of sampling. Three broad fractions of organic S have been characterized in soils: HI-reducible S, C-bonded S, and unidentified S (residual or inert). The HI-reducible S fraction contains S compounds that are not directly bonded to C and are believed to consist primarily of SO₄ esters, such as phenol SO₄, sulfated polysaccharides, choline SO₄ and sulfated lipids (Freney, 1967; Tabatabai and Bremner, 1972a; Chae and Tabatabai, 1981). Because the S in this fraction can be readily hydrolyzed to inorganic SO₄ by acid, HI-reducible S is considered to be the most labile fraction of organic S (Freney et al., 1975; Cooper, 1972). The C-bonded S is believed to consist largely of S in the form of S-containing amino acids such as methionine and cysteine. The C-bonded fraction is determined by reduction to H₂S with Raney nickel (Tabatabai, 1982).

Analyses of a wide range of soil shows that from 25 to 75% of the organic S in soil is HI-reducible, from 7 to 30% is C-bonded S and from 11 to 22% is unidentified (Tabatabai, 1984). The unidentified S may be in the form of aliphatic sulfones or aliphatic sulfonic acids that are not reduced to sulfide by either HI or Raney nickel (Freney, 1986). In short term greenhouse studies, Freney et al. (1975) reported that plants derived 60% of their S requirements from the C-bonded S fractions and the remaining 40% from the HI-reducible S fraction. This does not necessarily indicate

direct uptake of S from these fractions since microbial processes are involved in S transformation and it does not exclude the possibility that one fraction was converted to another during the course of these processes.

Inorganic soil S is present in primary minerals, and as elemental, sulfide, occluded (co-precipitated), and insoluble (precipitated) S, sulfate occurs in adsorbed forms and in soil solution (Metson, 1979). Several insoluble sulfates are possible in soils, including barium and strontium sulfates, sulfate as a co-crystallized impurity in calcium carbonate, and basic iron and aluminum sulfates. Some of these insoluble forms would not be recovered from soil by the methods used to extract adsorbed SO_4 and would be responsible for the possible overestimation of organic S content in the soil (Probert and Samosir, 1983). Although in aerobic environments, SO_4 dominates the inorganic S fraction in soil, under waterlogged conditions inorganic S occurs in reduced forms such as FeS, FeS_2 (pyrite) and H_2S (Mengel and Kirkby, 1978).

Analyses of the 37 surface soils of temperate regions by Tabatabai and Bremner (1972a) showed that the inorganic S represents only 1 to 5% of the total S and occurred entirely as SO_4 . SO_4 -S extracted from tropical soils by 0.1 M LiCl accounted for 1 to 9% and that extracted by a solution containing 500 mg P L^{-1} , P as Ca $(\text{H}_2\text{PO}_4)_2$ accounted for 5 to 23% of the soil total S (Neptune et al., 1975).

In the surface soils of tropical regions, Tabatabai and Bremner (1972b) reported a significant correlation of both total and organic S with organic C ($r=0.90$) and with total N ($r=0.87$). They further showed a significant relationship of ester SO_4 -S with total S ($r=0.89$), total N ($r=0.91$) and organic C ($r=0.82$); and carbon bonded S with total S ($r=0.77$), total N ($r=0.81$) and organic C ($r=0.89$). Neptune et al. (1975)

showed a significant correlation of total S content of the subtropical soil of Brazil with organic C ($r=0.85$) and total N ($r=0.88$).

For a tropical soil Acquaye and Kang (1987) obtained a significant correlation of total S with organic C ($r=0.85$), total N ($r=0.75$) and organic P ($r=0.66$).

Carbon, Nitrogen, Sulfur and Phosphorus Relationships in Soil

The relative proportion of C:N:Organic S is approximately 140:10:1.3 and does not vary greatly on a world-wide basis (Probert and Samosir, 1983).

Acquaye and Kang (1987) reported an average C:N, N:S, N:P, P:S, C:S and C:N:P:S ratio of 10.7:1, 6.8:1, 11.4:1, 0.7:1, 65.7:1 and 102:10:1:1.5, respectively, for the surface soils of tropical Ghana. Using the subtropical soils of Brazil, Neptune et al. (1975) reported an average C:N, N:P, N:S, P:S, and C:N:P:S ratio of 19.4, 11.2, 7.2, 0.9 and 194:10:1.2:1.6, respectively, and the corresponding averages for the temperate Iowa soils were 11.1, 7.3, 7.9, 1.1 and 110:10:1.4:1.3. The results obtained by Tabatabai and Bremner (1972b) for the average C:N, N:S, and C:N:S ratio of temperate region soil was also in close agreement with the value of Neptune et al. (1975).

Sulfur Transformations in Flooded Soils

Submergence of a soil creates unique chemical and biological conditions which markedly affect S transformations. When a soil is submerged the oxygen supply is drastically reduced which limits the rate of metabolism by soil microorganisms and the soil becomes anaerobic. Conversely, when oxygen supply from the atmosphere and

photosynthesis by algae and aquatic weeds exceeds oxygen consumption by soil organisms an oxidized zone develops in the upper part of the flooded horizon of soils. In flooded soils planted to rice, another oxidized zone develops in the rhizosphere, in addition to the oxidized surface layer. There is no sharp dividing line between the oxidized and reduced zones in a flooded soil.

The S transformations which occur in flooded soils are largely biological and the main reactions which take place are mineralization, immobilization, reduction of SO_4 , production of volatile S compounds and oxidation of elemental S and inorganic S compounds (Freney and Boonjawat, 1983).

Mineralization and Immobilization of Sulfur in Soil. Most of the S in agricultural soils is present in complex organic form. Since plants assimilate S almost entirely in the form of SO_4 , for organic S to become available to plants it has to be mineralized by microorganisms, which in turn is governed by the availability of energy sources in soil. Mineralization of S in soil is mainly biological and the amount of S mineralized in a given time depends on soil chemical and physical properties (Pirela and Tabatabaai, 1988). The opposing reactions of immobilization and mineralization occur simultaneously in soils and the net flux depends on the availability of energy and nutrients for microbial activity. During mineralization some of the released S is used for the synthesis of new cell material (immobilization) and that not required for synthesis is released as SO_4 .

Mineralization of S will occur in both aerobic and anaerobic zones but the inorganic species produced will be different in the two zones; SO_4 will be produced in

the aerobic zone and sulfide in the anaerobic zone. Immobilization of inorganic S also occurs in the aerobic and anaerobic zones with SO_4 being immobilized in the aerobic zone and sulfide in the anaerobic zone.

In studying the SO_4 release pattern over time, in soils amended with organic matter Barrow (1961), Nor (1981) and Tabatabai and Bremner (1972a) observed an immobilization of S during the initial stage of the study followed by SO_4 release. Williams (1967) and Tabatabai and Al-Khafaji (1980) found a steady linear release of SO_4 over the whole study period. Williams (1967) and Nor (1981) reported a rapid release of SO_4 during the first few days of incubation followed by a slower linear release.

It is considered that the conversion of organic S to inorganic S in soil is carried out mainly by microorganisms therefore any variable which affects the growth of microorganisms should affect the mineralization of S.

Mineralization of organic S is affected by a number of factors, such as temperature, pH, soil moisture, S concentration of the organic material, and the presence of plants. Optimum temperature for S mineralization is 30°C (Williams, 1967; Pirela and Tabatabai, 1988) with no mineralization occurring below 10°C . Above pH 7.0 S mineralization increases rapidly due to higher microbial activity and below pH 7.0 S mineralization is directly proportional to pH (Williams, 1967). Chaudhry and Cornfield (1967) reported 60% of field capacity as an optimum soil moisture for S mineralization. Mineralization of organic S was two and one-half to five times higher where soils were cropped as compared with fallow (Freney et al.,

1975). Sulfur was not released from plant material when the S concentration was less than 0.15% (Stewart et al., 1966).

If there is an abundant supply of carbon for energy then all of the available inorganic S will be immobilized into organic forms but if carbon is in short supply then inorganic S will probably be released from organic forms (Freney and Boonjawat, 1983).

Redox conditions can have significant effects on the incorporation of S into soil organic matter. Sachdev and Chhabra (1974) found that 37.8% of added inorganic SO_4 was converted to organic S under flooded conditions compared to the 28.1% incorporated under aerobic conditions.

Reduction of SO_4 . In aerated soil the main transformation of S is the oxidation of elemental S, sulfides and organic S compounds to SO_4 , whereas in flooded soil, SO_4 can be reduced to hydrogen sulfide which then reacts with iron, manganese, copper and zinc forming insoluble sulfides (Ponnamperuma, 1977). The reduction of SO_4 in soil under flooded conditions is due to the anaerobic respiration of facultative and obligate anaerobic organisms, because of the restricted oxygen supply. The rate of SO_4 reduction in flooded soils is dependent on soil properties (Ponnamperuma, 1972). Water soluble SO_4 in neutral and alkaline soils is reduced rapidly with time of submergence. But the acid soils first show an appreciable increase followed by a slow decline to a concentration of 1 mg S kg^{-1} soil at 16 weeks after flooding. SO_4 reduction in flooded soils follow first order reaction kinetics (IRRI, 1966) with velocity constants high in alkaline soils and low in acid soils.

Organisms mainly responsible for SO_4 reduction in soil under flooded conditions are bacteria of the genus *Desulfovibrio* and *Desulfotomaculum* (Starkey, 1966). Dissimilatory SO_4 reduction by microorganisms is a process in which SO_4 is used as terminal electron acceptor for the oxidation of organic compounds or hydrogen. The end products are sulfide ions or hydrogen sulfide gas which are excreted from the cells, while the assimilatory SO_4 reducers, such as plants, metabolize the products of SO_4 reduction (Freney and Boonjawat, 1983).

Sulfate is not reduced immediately after a soil is flooded. Following the flooding of a soil, oxygen disappears, and then nitrate, manganic compounds and ferric compounds are reduced before SO_4 (Ponnamperuma, 1977). The reduction of one component does not have to be complete before reduction of the next one can commence, but oxygen and nitrate must be removed before ferric ion and SO_4 are reduced. Generally sulfide accumulation in a flooded soil is promoted by the addition of organic matter (Abd-el-Malek and Rizk, 1963; Connell and Patrick, 1968).

Production of Volatile Sulfur Compounds. Several volatile organic S compounds are emitted from flooded soils. Among the compounds isolated in significant amounts are carbon disulfide, carbonyl sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide (Freney and Boonjawat, 1983).

Carbon disulfide is produced from the decomposition of the S containing amino acids, cysteine and cystine. Carbonyl sulfide is produced during the decomposition of Lanthiomine, djenkolic acid, thiocyanates and isothiocyanates (Banwart and Bremner, 1975). The principal sources of methyl mercaptan, dimethyl sulfide and dimethyl

disulfide seems to be the decomposition of methionine and related compounds, and sulfonium compounds (Freney and Boonjawat, 1983).

Hydrogen sulfide is produced in flooded soils as a result of SO_4 reduction or protein decomposition. However, the concentration of water soluble hydrogen sulfide seems to be extremely low under most conditions due to its reaction with ferrous iron and other cations to form insoluble sulfides (Connell and Patrick, 1969).

Arylsulfatase Activity of Soils

It is generally accepted that S is taken up by plant roots as SO_4 , which is produced by mineralization of soil organic S (Williams, 1975). Sulfatases are enzymes that hydrolyze organic SO_4 esters ($\text{R-O-SO}_3^- + \text{H}_2\text{O} = \text{R-OH} + \text{H}^+ + \text{SO}_4^{2-}$) and may play an important role in the processes by which soil organic S is mineralized and made available for plant growth (Freney, 1967).

Several types of sulfatases occur in nature. They have been classified according to the type of organic SO_4 esters they hydrolyze, with the following main groups recognized: arylsulfatase, alkylsulfatase, steroid sulfatases, glucosulfatases, chondrosulfatases, and myrosulfatases (Roy, 1960).

Arylsulfatase hydrolyzes SO_4 esters with an aromatic radical (phenolic esters of sulfuric acid) and were originally described as phenolsulfatase (Tabatabai and Bremner, 1970a). The arylsulfatase activity has been found to be associated with the organic fraction. Appiah and Ahenkorah (1989) found that arylsulfatase activity was correlated positively and significantly with organic C, total N and cation exchange capacity, and correlated negatively with acetate soluble SO_4 . Arylsulfatase activity in some

temperate Iowa soils was correlated with organic C and activity decreased with depth in the profile as organic matter decreased (Tabatabai and Bremner, 1970b). Arylsulfatase activity has also been found to be related to organic matter, total N, total S and with ester SO_4 in soils (Cooper, 1972; Lee and Speir, 1979).

Adsorption of SO_4 by Soils

In the tropics highly weathered soils containing Fe and Al oxides and kaolinitic clay can adsorb large amounts of SO_4 but this decreases with increasing soil pH and phosphorus level (Kamprath and Till, 1983; Fox et al., 1971). In cultivated soils SO_4 adsorption is primarily in the B horizon, especially in soils that have been limed or treated with phosphorus and S fertilizers. Sulfate adsorption is concentration dependent. The higher the external concentration of SO_4 , the greater the amount of SO_4 adsorbed.

Couto et al. (1979) observed that less than 50% of the SO_4 adsorbed by the B2 horizon of an oxisol from Brazil could be desorbed by extracting with NH_4NO_3 solution, while all of the SO_4 adsorbed by the Ap horizon was desorbed. This suggests that the B horizons of highly weathered soils in the tropics have an appreciable number of sites where SO_4 is held very strongly. The adsorbed SO_4 in the B horizons can be an important source of plant available SO_4 providing it can be reached and released for plant uptake.

The most important difference between tropical and temperate soils lies in the adsorbed:soluble SO_4 ratio. Weathered tropical soils generally have a higher amount of

pH dependent charge and a higher AEC than temperate soils, and hence a greater capacity to adsorb anions such as SO_4 (Blair and Lefroy, 1987).

The capacity of soils to adsorb SO_4 is dependent on a number of physical and chemical properties. The amount of SO_4 retained or adsorbed by a soil increases with clay content (Chao et al., 1962). Sulfate is considered to be held in soils with the anion adsorption strength in the order of: $\text{OH} > \text{H}_2\text{PO}_4 > \text{MoO}_4 > \text{SO}_4 = \text{CH}_3\text{CO}_2 > \text{NO}_3 > \text{Cl}$ (Harward and Reisenaur, 1966). Retention of SO_4 decreases as the pH increases and adsorption appears to be negligible in many soils when pH is above 6.5 (Harward and Reisenauer, 1966; Tabatabai and Bremner, 1972a).

Little information is available on the SO_4 adsorption capacities of wetland rice soils of Bangladesh.

Microbial Biomass Sulfur in Soils

Biological approaches are receiving increasing attention by investigators to measure the dynamics of nutrient transformations in soils. Studies on the transformations of organic S to inorganic forms in soil, indicate that a relatively small fraction of the total S is involved at any one time. McLaren et al. (1985) estimated the active pool in both unamended and glucose amended soils to be about 3 to 6% of the total S and of a similar magnitude to the inorganic S pool. Using ^{35}S -labelled gypsum Goh and Gregg (1982) found that 90 to 95% of the total soil S was not involved in cycling and part of the remaining S was inorganic SO_4 .

Microbial biomass S is an important fraction of the soil organic S. Although the microbial mass contains only a small proportion of soil S, this fraction is extreme-

ly labile and is thought to be the key to understanding S turnover in soil (Biederbeck, 1978). Saggar et al. (1981) found microbial biomass S in soil accounted for about 2.5% of the total soil S. Strick and Nakas (1984) reported similar values of 1.2 and 2.2% for two acid organic soils. In estimating the microbial biomass S in low S status soils of Scotland that respond to fertilizer S, Chapman (1987) found that biomass S exceeded the extractable plant available S. These results suggest that microbial biomass S can form a significant proportion of the organic S pool which is involved in S cycling and is potentially available to plants.

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CHAPTER I

EFFECT OF ORGANIC RESIDUE AMENDMENTS ON THE MINERALIZATION OF SULFUR IN FLOODED RICE SOILS

ABSTRACT

This study was undertaken to assess the mineralization of S in flooded rice soils amended with organic residues. Three rice soils (Joydebpur, Faridpur and Thakurgaon) were amended with three levels of organic residues: 1) control, 2) rice straw (*Oryza sativa* L.) and 3) pea vine (*Pisum sativum* L.). Organic residues (25 mg g⁻¹ soil) were added to the soil and mixed with soil and glass beads (1:1, soil to bead ratio) and transferred into a pyrex leaching tube. Soils were kept flooded and incubated at 35°C and leached with deionized water at 1, 2, 4, 8, and 12 weeks to measure SO₄ and other chemical properties of the soil. Potentially mineralizable S pool (S₀) and C pool (C₀) and first-order rate constants (K_S for S and K_C for C) in soils amended with rice straw and pea vine under flooded conditions were estimated using the exponential equation of Stanford and Smith (1972). The S₀ and K_S varied considerably among the soils and types of added organic residues. The S₀ and K_S values in rice straw and pea vine ranged from 8.70 to 29.55 mg S kg⁻¹ soil and 0.124 to 0.732 mg S kg⁻¹ wk⁻¹, respectively. Except for Thakurgaon soil, the S₀ and K_S values in Joydebpur and Faridpur soils were higher in the unamended treatments. Higher S₀ values in the unamended soils were probably due to less microbial activity in these soils to mineralize organic S from organic residues. This implies from the results that the amount of SO₄ in flooded soils amended with organic residues is dependent on soil type, nature of organic residues, and time of incubation. The C₀ and K_C values under flooded incubation showed higher C₀ values and K in residue

amended soils compared to unamended soils. Among the two residues, pea vine treated soils had higher C_0 and K_C values than the soils treated with rice straw.

INTRODUCTION

Rice is the most important crop in Asia, where more than 80% of the world's rice is grown and consumed, and there is mounting pressure to increase yields. In recent years sulfur (S) deficiency is recognized as a major constraint to the agricultural system in many tropical areas of the world (IFDC, 1979).

Since most rice production utilizes flooded soil, submergence of a soil creates unique chemical and biological conditions which markedly affect S transformations (Freney and Boonjawat, 1983). The availability of S to rice plants under such flooded conditions is greatly reduced due to the reduction of sulfate to sulfide.

Sulfur in agricultural soils occurs both in organic and inorganic form, with organic S accounting for more than 95% of the total soil S (Tabatabai, 1984). It is generally accepted that plants assimilate S almost entirely in the form of sulfate, which is produced by the mineralization of soil organic S (Williams, 1975). Therefore, S mineralization rates (K) and potentials (S_0) are important parameters in predicting plant nutritional needs and the amount of S fertilizer needed for optimum crop yield (Pirela and Tabatabai, 1988).

Mineralization of S in soils is mainly biological in nature, and the amount of S mineralized in aerobic soils in a given time depends on soil chemical and physical properties (Pirela and Tabatabai, 1988) and type of organic residues added to soils (Tabatabai and Chae, 1991). Using the leaching incubation tube technique, originally proposed by Standford and Smith (1972) to study the N mineralization potentials of

soils, Tabatabai and Al-Khafaji (1980) found a linear relationship between the cumulative amount of S mineralized and time of incubation in aerobic soils.

However, very little information is available on the mineralization of S in wetland rice soils. Therefore, the objective of this study was to assess the effect of added organic residues on the potentially mineralizable S pool and first-order rate constants of some wetland rice soils under flooded conditions.

MATERIALS AND METHODS

The soils used in this study (Table 1.1) were surface (0-15 cm) soils selected to represent the large rice growing areas of Bangladesh. Samples of field moist soils were collected, air-dried, crushed and passed through a 2-mm screen, placed in a polyethylene bag and stored in a plastic air-tight container. A subsample of the air-dried soils was ground to pass a 100-mesh sieve for determination of the chemical properties.

Analytical Procedures

The pH was determined by a glass electrode (soil/water ratio, 1:2.5), and total organic C in the soil by combustion and infrared detection on a carbon analyzer (Dohrman, Santa Clara, CA). Total C in organic residues were measured by LECO WR-12 carbon analyzer (LECO Corp., St. Joseph, MI).

Total S was measured by the methylene blue color method after digestion with NaOBr and reduction to H₂S with hydriodic acid (HI) acid using Johnson-Nishita

distillation units (Tabatabai and Bremner, 1970a). Soil SO_4 was extracted with 0.1 M LiCl solution (Roberts and Koehler, 1968); or 500 mg P L^{-1} (Fox et al., 1964), or 100 mg P L^{-1} solution as monocalcium phosphate (Dick and Tabatabai, 1979) and measured on a Dionex ion chromatograph (Sunny Vale, CA). Hydriodic acid reducible S was determined by using Johnson and Nishita distillation unit (Tabatabai, 1982). Ester S was calculated by subtracting calcium phosphate (100 mg P L^{-1}) extractable SO_4 -S from HI-reducible S. C-bonded S was determined by distillation with Raney-Ni alloy (Lowe and Delong, 1963). Reduced S was measured by Zn-HCl reduction method of Aspiras et al. (1972). Residual S was determined by difference as follows:

Residual S = Total S - HI reducible S - Raney-Ni reducible S - Zn-HCl reduced S.

Total N was determined by the semimicro-Kjeldahl digestion followed by steam distillation and titration (Bremner, 1970). Nitrates and ammonium were extracted by calcium phosphate (100 mg P L^{-1}) (Dick and Tabatabai, 1979) and analyzed by ion chromatography and steam distillation (Bremner and Keeney, 1965), respectively. Total P was measured by alkaline oxidation (Dick and Tabatabai, 1977). Water extractable phosphate was determined colorimetrically (Olsen and Sommers, 1982).

Arylsulfatase enzyme activity was determined by using *p*-nitrophenyl sulfate as the substrate and measurement of the product *p*-nitrophenol (PNP) (Tabatabai and Bremner, 1970b). Particle size distributions were determined in the <2 mm sample by hydrometer method (Gee and Bauder, 1986).

Incubation Procedures

An incubation study was carried out with three soils and three organic residue treatments. The organic residue treatments were 1) control, 2) rice straw (*Orzya sativa* L.), and 3) pea vine (*Pisum sativum* L.). Thirty g air-dried soil (2-mm sieved) and an equal weight of glass beads (0.45 to 0.52 mm in diameter) and 0.75 g (25 mg⁻¹ soil) of each organic residues were mixed thoroughly and transferred into a Pyrex leaching tube (42 mm diameter by 160 mm length). Glass beads were used instead of silica sand to avoid the contamination of S. The soil-glass beads mixture was retained in the leaching tube by means of a glass wool pad in the bottom of the leaching tube. The glass wool pad was covered by a thin layer of glass beads. Soils were incubated at 35°C in an incubator and were kept flooded by adding 50 ml deionized (DI) water in each leaching tube.

During the incubation the leaching tubes were placed in an upright position in a rack and covered with clear plastic film. To determine chemical content of soil solution the soil:glass beads mixture was leached with 100 ml deionized water in five increments by using vacuum manifold. Soil:glass beads mixtures were leached carefully so that soils remained flooded.

The soils were kept flooded for 12 weeks with the leaching at 1, 2, 4, 8, and 12 weeks. The efficiency of leaching SO₄ with deionized (DI) water or 0.01 M KCl solution was tested. Results showed that the amount of S extracted by DI water and 0.01 M KCl were significantly correlated to each other ($R^2 = 0.98$) and therefore DI water was the method employed in the S mineralization study. The moisture content

of the leaching columns was adjusted by weighing the columns on alternate days adding DI water as needed.

The leachate was analyzed for: $\text{SO}_4\text{-S}$ by ion chromatography for the first week, and for the remaining periods leachate was concentrated in a 50 mL distillation flask by drying in an oven at 70°C followed by $\text{SO}_4\text{-S}$ determination by HI acid distillation (Johnson and Nishita, 1952); total soluble C and soluble organic C by Dohrman carbon autoanalyzer, and iron and manganese content by Atomic Absorption. The pH and Eh of the flooded soils were measured directly in the incubation leaching tube just before collection of the leachate by glass combination electrode and platinum redox electrode, respectively.

All incubations were carried out in duplicate. The analyses reported are the averages of duplicate determinations.

The exponential equation proposed by Stanford and Smith (1972) for cumulative N mineralization potential (N_0) and first order rate constant (K) was used to solve the following equation for potentially mineralizable S pool S_0 and first order rate constants (K_s).

$$S_m = S_0[1 - \exp(-K_s t)]$$

where S_m = amount of S mineralized at specific time (t).

Potentially mineralizable C pool C_0 and rate constant K_C was also estimated by the same method.

RESULTS AND DISCUSSION

pH and Eh

The pH of the two acid soils Joydebpur and Thakurgaon (Figs. 1.1 and 1.3) increased rapidly at the first two weeks of flooding, followed by gradual increase up to 12 weeks. Conversely, the alkaline soils, Faridpur, decreased from a pH of 8.17 to 7.50 within the first two weeks and maintained that level up to 12 weeks of incubation period (Fig. 1.2). Addition of rice straw or pea vine only affected the pH of Faridpur soil which caused a greater depression in pH than the unamended control. At 12 weeks the pH values of all incubated soils ranged from 7.40 to 7.52. The stable pH values obtained at 12 weeks were in close agreement with the report of Ponnampervuma (1965).

The Eh of the soils at start of the incubation (0 week) ranges from +111 to +204 mV (Figs. 1.4 to 1.6). Flooding drastically reduced the soil Eh values at 12 weeks ranging from -197 to -282 mV. The Eh values obtained supports the report of Ponnampervuma (1972) that Eh stabilized (+200 to -300 mV) in soil after several weeks of submergence. Addition of organic residues showed no significant effect on Eh except for the Thakurgaon soil where pea vine and rice straw maintained higher Eh values than the control.

Mineralization of Sulfur

The relationship between cumulative values of S in soils amended with organic residues and time of incubations are shown in Figures 1.7, 1.8 and 1.9. Except for the

Thakurgaon soil treated with pea vine, the cumulative S values in Joydebpur and Thakurgaon soils treated with rice straw or pea vine were considerably lower than the control treatment. Lower cumulative values of S in Joydebpur and Faridpur soils treated with organic residues under flooded incubation may be partially due to low Eh values of the soils (Figs. 1.4 and 1.5) and high water-soluble iron (Fe^{2+}) and manganese (Mn^{2+}) content (Table 1.3 and 1.4), compared to control treatment. Lower Eh values in soil cause greater reduction of SO_4 to hydrogen sulfide. The hydrogen sulfide thus formed reacts with reduced iron compound and produce insoluble FeS (Ponnamperuma, 1977).

The Thakurgaon soil produced unexpected results because pea vine with a C:S ratio of 284 had net S mineralization but rice straw with a narrow C:S ratio of 63 apparently had net immobilization of S. Also it showed a similar soil C:S ratio to the Joydedpur soil, suggesting some other unique aspect of the Thakurgaon soil such as soil biology may be playing a role in S mineralization.

Using the exponential equation of Standford and Smith (1972) the potentially mineralizable S pool (S_0) and first-order rate constants (K_s) were estimated (Table 1.5). In calculating the S mineralization constants the initial S values were subtracted from the cumulative S values.

The K_s values for unamended soils ranged from 0.553 to 0.630 $\text{mg S kg}^{-1} \text{wk}^{-1}$, and those of soils treated with pea vine were from 0.270 to 0.732 $\text{mg S kg}^{-1} \text{wk}^{-1}$. Soils treated with rice straw had the lowest K_s values ranging from 0.124 to 0.430 $\text{mg kg}^{-1} \text{wk}^{-1}$. The K_s values thus obtained under unamended, flooded soils were higher

than the Chilean field moist soils which range from 0.06 to 0.25 mg S kg⁻¹ wk⁻¹ (Pirela and Tabatabai, 1988).

In the two acid soils, rates of mineralization (K_s) were lower with the rice straw than with the pea vine. A possible explanation is that the rice straw had a much greater amount of C-bonded S added than the pea vine (Table 1.2). There may have been greater reduction of C-bonded S directly to sulfide. Freney (1967) and Stevenson (1986) reported that C-bonded S in cysteine is directly converted to H₂S during anaerobic decomposition of organic residues.

Except for the Thakurgaon soil, the S_0 values of unamended Joydebpur and Faridpur soils were much greater than the rice straw or pea vine treated counterparts, suggesting less microbial activity in these soils (Table 1.3) to mineralize organic S from organic residues. Tabatabai and Chae (1991) had similar results which showed that under aerobic conditions there was a net immobilization or mineralization as a function of soil type. Values of S_0 for unamended soils ranged from 14.40 to 24.73 mg S kg⁻¹ soil, which was somewhat lower than that reported by Pirela and Tabatabai (1988) who found S_0 values of 21 to 47 mg S kg⁻¹ soil at 30°C for Chilean field moist aerobic soils.

Carbon Mineralization

The potentially mineralizable C pool (C_0) and rate constants (K_C) are shown in Table 1.6. The K_C values for unamended soils ranged from 0.39 to 0.79 mg C kg⁻¹ wk⁻¹. The rate constants for rice straw and pea vine treated soils were approximately 4 to 7 times more than those obtained for unamended soils (Table 1.4). Among the two

organic residue treatments, soils treated with pea vine had the highest cumulative amount of mineralized C (Figs. 1.10, 1.11 and 1.12) C_0 and K values. The C_0 values of residue treated soils ranged from 1.83 to 4.50 mg C kg⁻¹ soil and K_C values were from 1.21 to 2.06 mg C kg⁻¹ wk⁻¹. For decomposition of alfalfa under anaerobic conditions Gale and Gilmour (1988) reported C mineralization (sum of CO₂, CH₄ and water soluble C) rate (K_C) values of 0.826 and 0.168 mg C kg⁻¹ wk⁻¹, during initial and intermediate phases, respectively. The pea vine may have had the higher K_C and C_0 values because C was in excess (ie. N and S were limiting). In addition, rice straw may contain higher amounts of resistant material, such as lignin, resulting in lower C_0 and K_C values compared to pea vine.

Correlation Between Soil Properties and S Mineralization Parameters Under Flooding

The matrix of correlation coefficients (r) between various properties of soils measured over 12 weeks flooded incubation are shown in Tables 1.7 to 1.9.

The pH and Eh of all three soils showed a highly significant correlation to each other ($P < 0.001$). Sulfate-S content of Joydebpur and Faridpur soils were significantly correlated to soil pH and Eh. Cumulative SO₄-S in Joydebpur and Thakurgaon soil were positively correlated but Faridpur soil was negatively correlated to soil pH. Cumulative SO₄-S in all the soils incubated under flooded conditions were significantly, but negatively, correlated to soil Eh. Only SO₄-S content of Thakurgaon soil showed significant correlation to soluble organic carbon (SOC) content of the soils.

CONCLUSION

Potentially mineralizable S pool (S_0), C pool (C_0) and rate constants (K_s for S and K_C for C) in soils amended with rice straw and pea vine under flooded conditions were estimated using exponential equation of Stanford and Smith (1972). The S_0 and K_s values varied considerably among the soils and types of organic residue added. Higher S_0 values in the unamended Joydebpur and Faridpur soils suggests poor microbial activity in these soils to mineralize organic S from organic residues. Results of this study shows that S mineralization under flooded conditions amended with organic residues are dependent on soil type, nature of organic residues, and time of incubation.

The C_0 and K_C values under flooded incubation showed higher C_0 values and rate constants (K) in residue amended soils compared to unamended soils. Among the two residues, pea vine treated soils had highest C_0 and K_C values than the soils treated with rice straw. High C_0 and K_C values in pea vine treated soils were probably due to excess C content and larger content of easily biodegradable organic constituents when compared with rice straw.

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Table 1.1. Physical and chemical properties of the Bangladesh soils used in the incubation study.

Parameters	Soil		
	Joydebpur	Faridpur	Thakurgaon
Soil Order	Ultisol	----	Ultisol
Particle size			
sand (%)	7.4	5.2	25.9
silt (%)	47.3	59.8	47.4
clay (%)	45.3	35.0	26.7
USDA Textural class	silt loam	silty clay loam	clay loam
pH	6.62	8.17	5.83
Total Organic C (g kg ⁻¹)	11.0	14.4	10.4
Total S (mg kg ⁻¹)	138.8	136.5	131.5
Extractable SO ₄ -S			
CaP ₅₀₀ (mg kg ⁻¹)	8.97	7.61	3.91
CaP ₁₀₀ (mg kg ⁻¹)	8.85	7.62	2.62
LiCl [†] (mg kg ⁻¹)	7.06	7.36	2.41
Ester (S mg kg ⁻¹)	44.7	79.6	62.4
C-bonded S (mg kg ⁻¹)	36.2	20.5	17.5
Reduced S (mg kg ⁻¹)	2.70	1.96	5.83
Residual S (mg kg ⁻¹)	46.2	26.8	42.8
Arylsulfatase Activity			
mg PNP‡ (kg ⁻¹ hr ⁻¹)	70.9	41.4	35.1
Total N (mg kg ⁻¹)	990	830	980
1.6mM CaP Extractable			
NH ₄ -N (mg kg ⁻¹)	16.62	10.01	9.40
NO ₃ -N (mg kg ⁻¹)	4.92	34.35	4.74
Total P (mg kg ⁻¹)	379	748	449
Water soluble			
PO ₄ -P (mg kg ⁻¹)	0.83	1.01	2.25

[†]0.1 M LiCl solution.

‡ p-nitrophenol.

Table 1.2. Chemical properties of the organic residues used in the incubation study.

Properties	Rice straw (IR36)	Pea vine (mature) [†]
Total Organic C (g kg ⁻¹)	405	403
Total S (g kg ⁻¹)	6.44	1.42
Total N (g kg ⁻¹)	29.2	13.3
Total P (g kg ⁻¹)	7.4	1.6
C:S ratio	63	284
C:N ratio	13.9	30.3
C:P ratio	55	252
N:S ratio	4.53	9.37
HI reducible S (mg kg ⁻¹)	5428	835
C-bonded S (mg kg ⁻¹)	82	14
Reduced S (mg kg ⁻¹)	23.2	6.6
Residual S (mg kg ⁻¹)	907	564

[†]Pods removed.

Table 1.3. Cumulative amount of water soluble iron (Fe^{2+}) in soils amended with organic residues and incubated under continuous flooding condition.

Residue Treatments	Weeks				
	1	2	4	8	12
	mg Fe^{2+} kg ⁻¹ soil				
<u>Joydebpur Soil</u>					
Control	0.14	0.24	0.42	1.17	1.94
Rice straw	4.42	4.89	5.73	6.18	6.68
Pea vine	1.32	2.12	2.22	2.36	3.27
<u>Faridpur Soil</u>					
Control	0.17	0.36	0.55	1.02	1.34
Rice straw	2.27	3.21	3.34	3.49	4.13
Pea vine	6.33	7.98	8.11	8.23	8.32
<u>Thakurgaon Soil</u>					
Control	0.22	0.74	1.02	1.59	1.95
Rice straw	2.87	4.05	4.36	4.76	6.27
Pea vine	6.00	9.23	11.91	12.37	13.49

Table 1.4. Cumulative amount of water soluble manganese (Mn^{2+}) in soils amended with organic residues and incubated under continuous flooding condition.

Residue Treatments	Weeks				
	1	2	4	8	12
mg Mn^{2+} kg ⁻¹ soil					
<u>Joydebpur Soil</u>					
Control	0.23	0.36	0.42	0.42	0.42
Rice straw	5.39	9.39	11.09	11.47	11.85
Pea vine	7.27	10.70	12.02	12.06	12.29
<u>Faridpur Soil</u>					
Control	0.12	0.32	0.36	0.36	0.36
Rice straw	4.32	5.97	6.65	6.69	6.85
Pea vine	3.20	4.73	5.15	5.17	5.30
<u>Thakurgaon Soil</u>					
Control	0.12	0.24	0.28	0.30	0.30
Rice straw	1.17	1.59	1.89	1.93	2.02
Pea vine	3.98	4.50	4.67	4.67	4.70

Table 1.5. Sulfur mineralization constants[†] for soils amended with organic residues and incubated under continuous flooding condition.

Residue Treatments	S ₀	K _s	R ² [‡]
<u>Joydebpur Soil</u>			
Control	15.5	0.613	0.94
Rice straw	13.31	0.124	0.95
Pea vine	11.22	0.270	0.92
<u>Faridpur Soil</u>			
Control	24.73	0.553	0.96
Rice straw	12.18	0.430	0.97
Pea vine	8.70	0.392	0.90
<u>Thakurgaon Soil</u>			
Control	14.40	0.630	0.96
Rice straw	16.14	0.283	0.83
Pea vine	29.55	0.732	0.87

[†]S₀ = potential mineralizable S (mg S kg⁻¹ soil) and K_s = first-order rate constant (mg S kg⁻¹ wk⁻¹).

[‡]Significant at P < 0.05.

Table 1.6. Carbon mineralization constants[†] for soils amended with organic residues and incubated under continuous flooding condition.

Residue Treatments	C ₀	K _C	R ² [‡]
<u>Joydebpur Soil</u>			
Control	0.48	0.317	0.92
Rice straw	1.87	1.214	0.94
Pea vine	2.94	2.019	0.98
<u>Faridpur Soil</u>			
Control	0.39	0.260	0.97
Rice straw	1.83	1.402	0.94
Pea vine	2.61	1.909	0.98
<u>Thakurgaon Soil</u>			
Control	0.79	0.308	0.96
Rice straw	2.66	1.578	0.96
Pea vine	4.50	2.064	0.92

[†]C₀ = potential mineralizable C (mg C kg⁻¹ soil) and K_C = first-order rate constant (mg C kg⁻¹ wk⁻¹).

[‡]Significant at P < 0.05.

Table 1.7. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Joydebpur soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	SO ₄ -S	Cum SO ₄ -S [§]
pH	--	-0.95 ^{***}	0.09	0.21	-0.83 ^{***}	0.69 ^{**}
Eh		--	-0.19	-0.39 [*]	0.80 ^{***}	-0.62 ^{***}
SOC			--	0.74 ^{***}	-0.26	-0.33
HCO ₃				--	-0.35 [*]	-0.37 [*]
SO ₄ -S					--	-0.48 ^{**}
cum SO ₄ -S						--

^{*,**,***}Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]cum SO₄-S = cumulative SO₄-S.

Table 1.8. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Faridpur soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	SO ₄ -S	Cum SO ₄ -S [§]
pH	--	0.86 ^{***}	-0.15	-0.19	0.68 ^{***}	-0.46 ^{**}
Eh		--	-0.18	-0.31	0.59 ^{***}	-0.59 ^{***}
SOC			--	0.85 ^{***}	-0.28	-0.33 [*]
HCO ₃				--	-0.20	-0.33 [*]
SO ₄ -S					--	-0.15
cum SO ₄ -S						--

^{*, **, ***}Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]cum SO₄-S = cumulative SO₄-S.

Table 1.9. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Thakurgaon soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	SO ₄ -S	Cum SO ₄ -S [§]
pH	--	-0.93 ^{***}	0.11	0.29	0.05	0.63 ^{***}
Eh		--	-0.04	-0.28	0.05	-0.48 ^{**}
SOC			--	0.57 ^{***}	0.58 ^{***}	-0.08
HCO ₃				--	0.22	-0.16
SO ₄ -S					--	0.16
cum SO ₄ -S						--

^{***}Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]cum SO₄-S = cumulative SO₄-S.

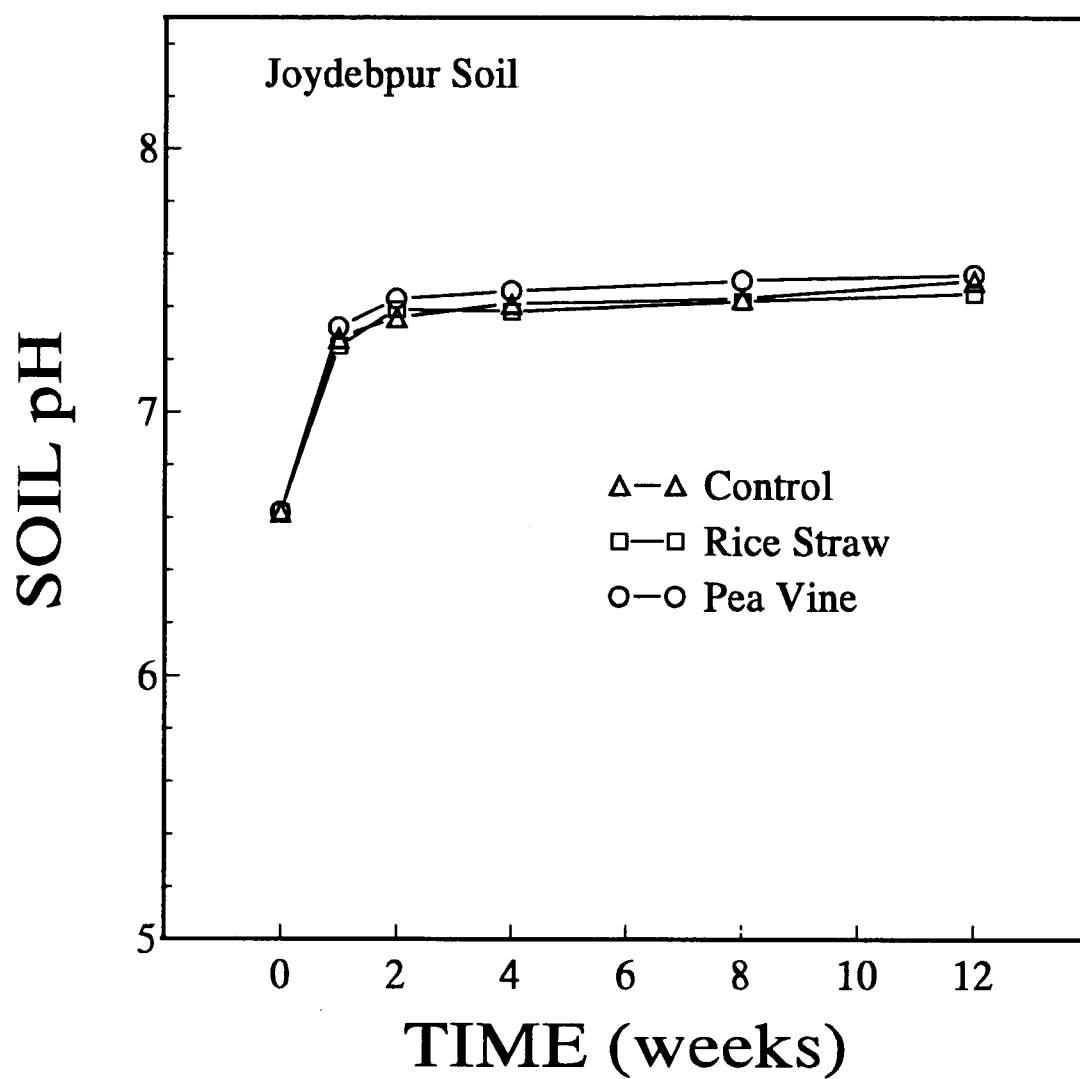


Figure 1.1. Effect of added organic residues on the pH of a Joydebpur soil incubated under flooded conditions.

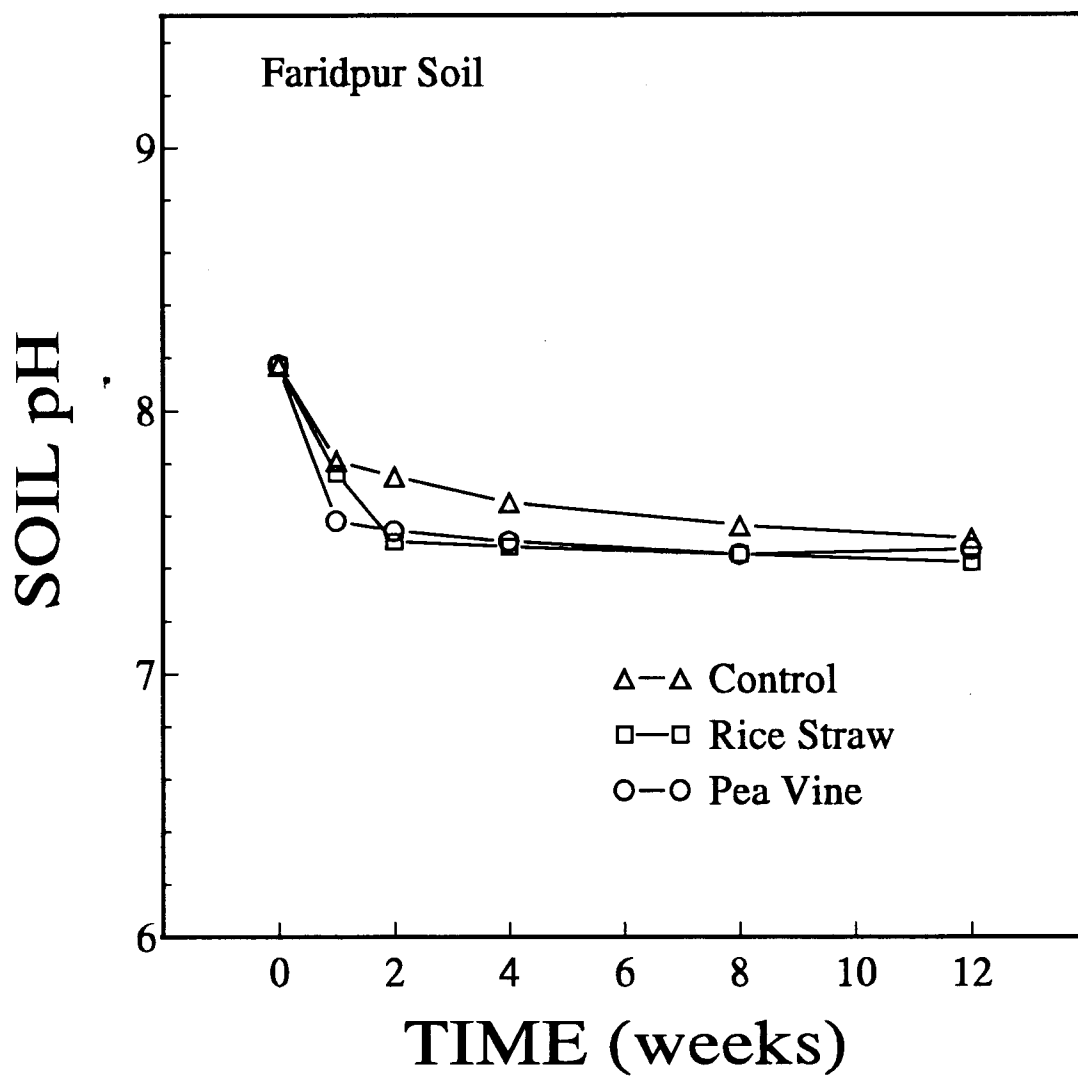


Figure 1.2. Effect of added organic residues on the pH of a Faridpur soil incubated under flooded conditions.

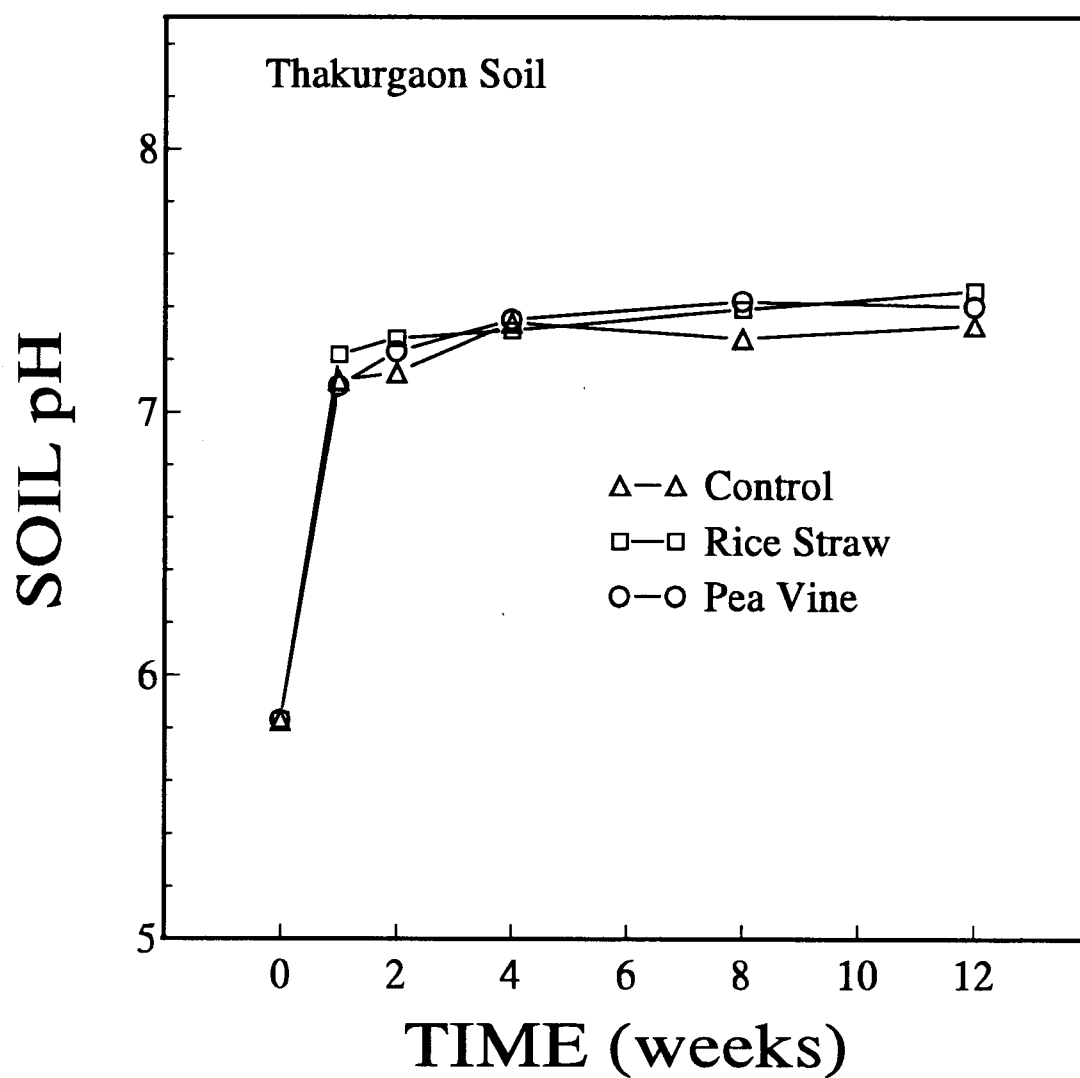


Figure 1.3. Effect of added organic residues on the pH of a Thakurgaon soil incubated under flooded conditions.

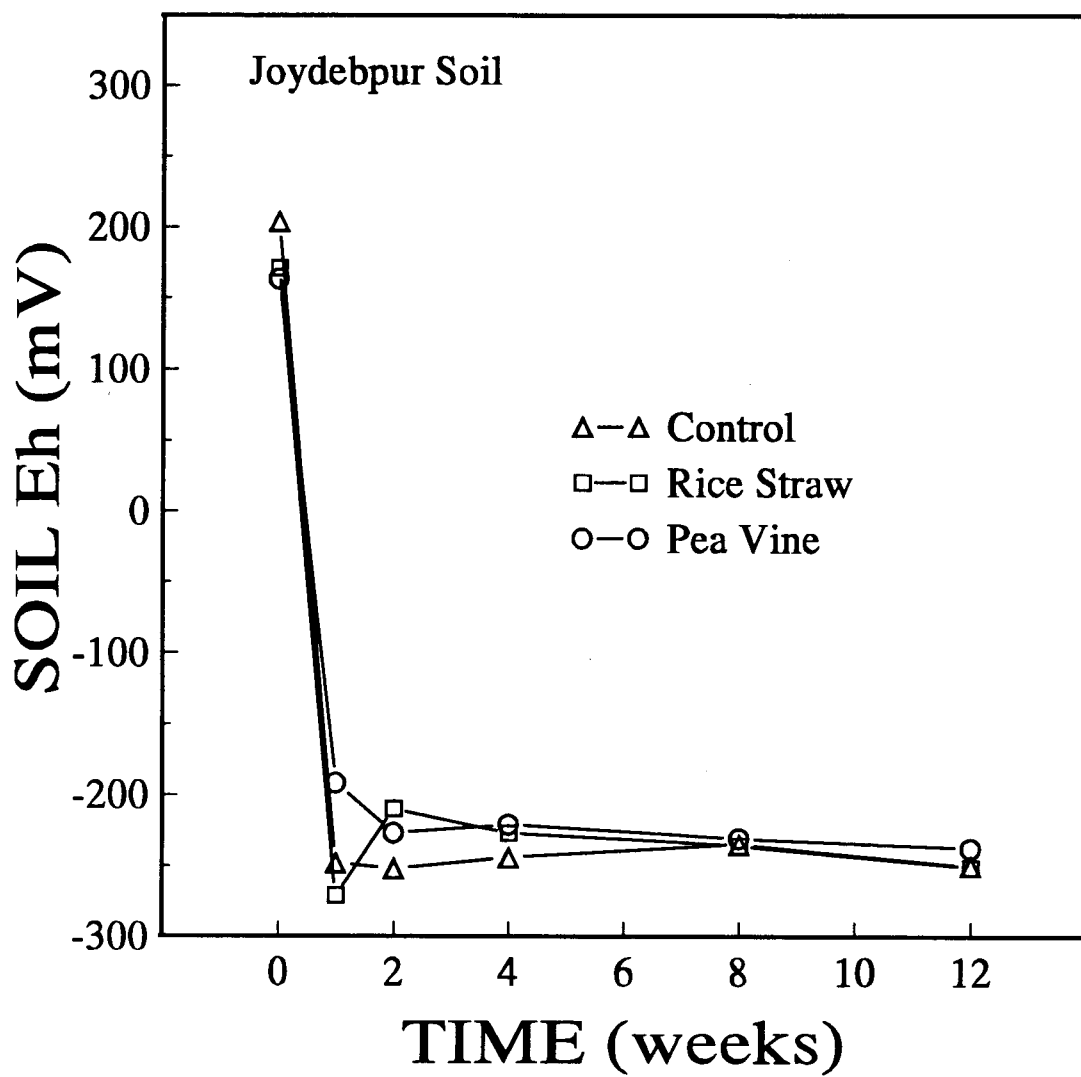


Figure 1.4. Effect of added organic residues on the Eh of a Joydebpur soil incubated under flooded conditions.

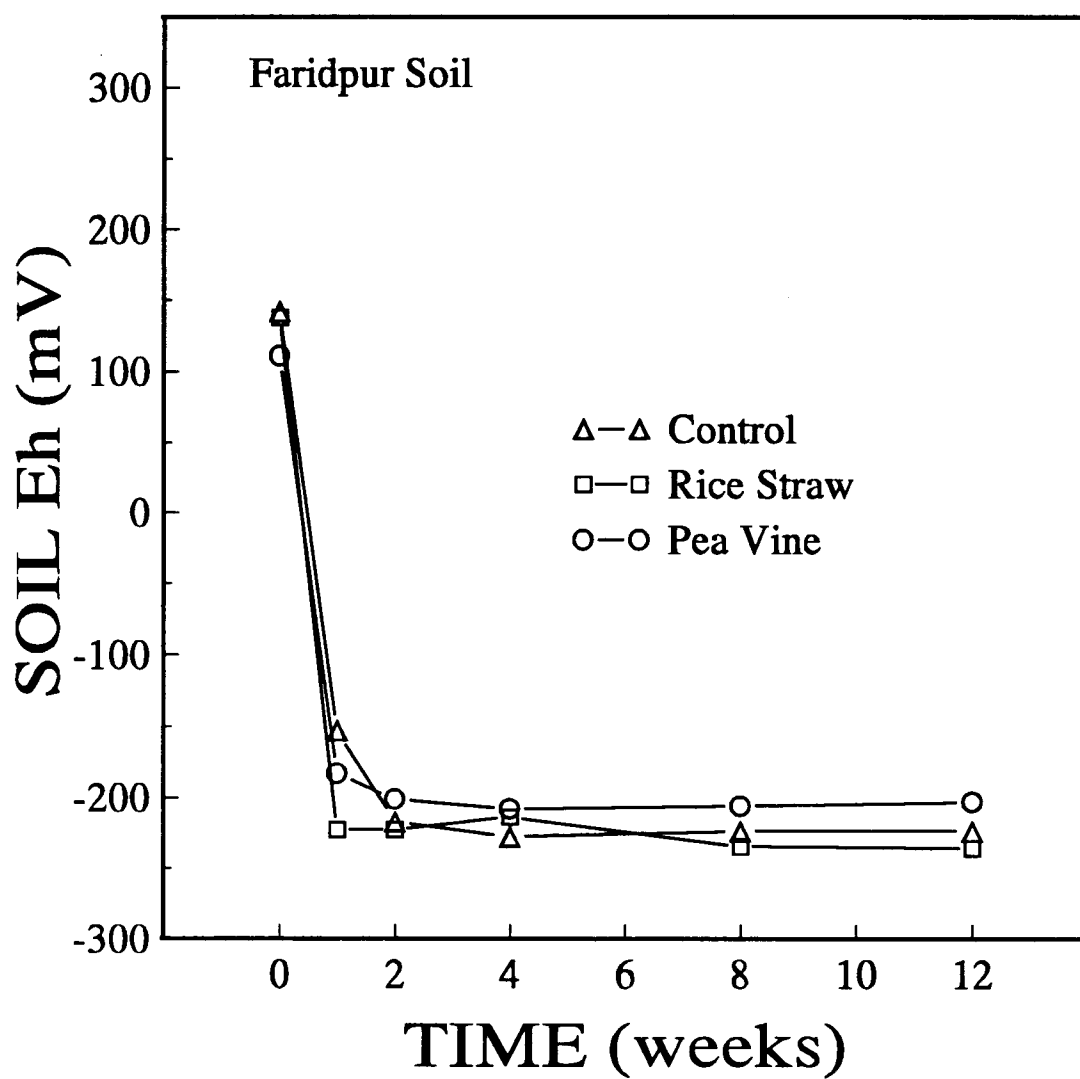


Figure 1.5. Effect of added organic residues on the Eh of a Faridpur soil incubated under flooded conditions.

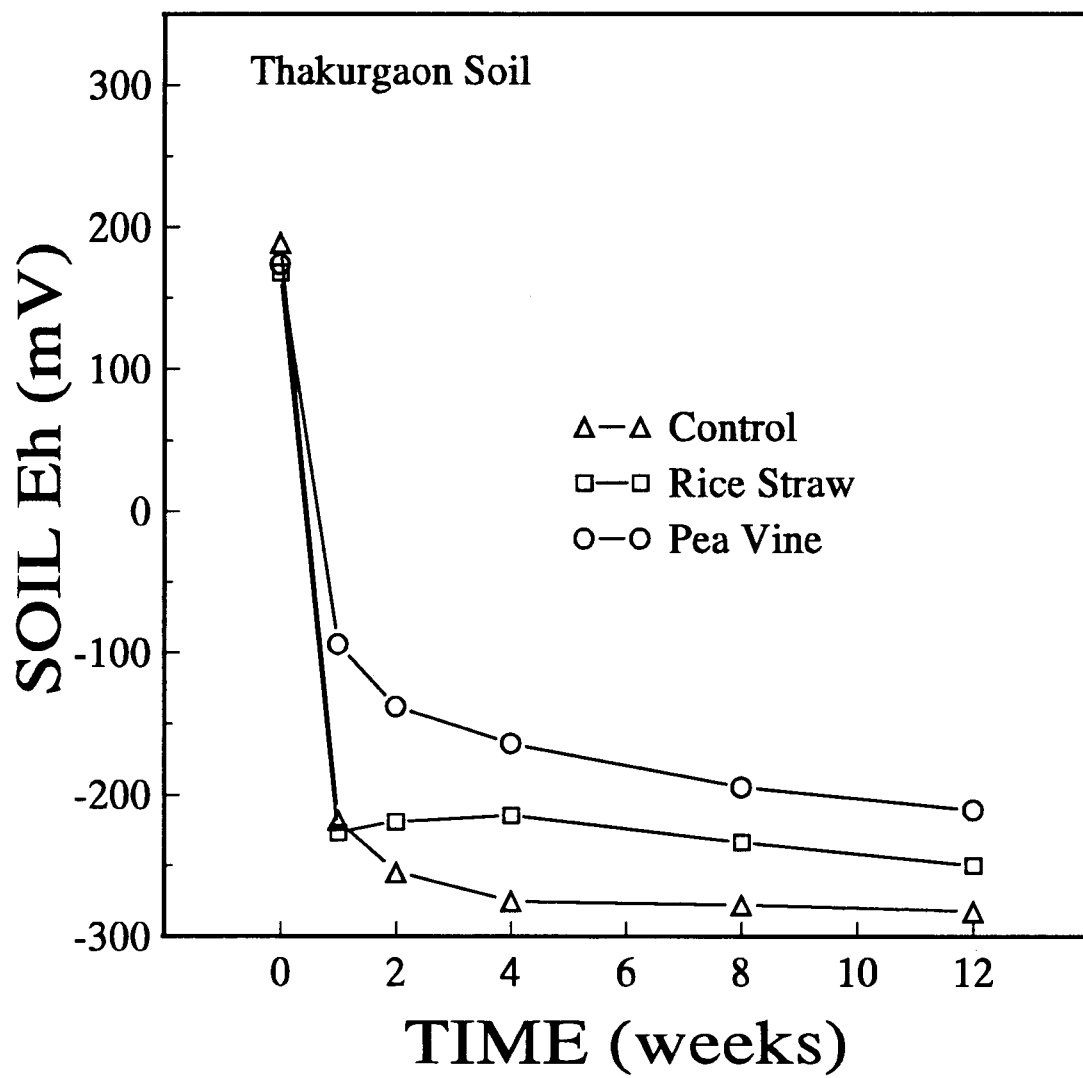


Figure 1.6. Effect of added organic residues on the Eh of a Thakurgaon soil incubated under flooded conditions.

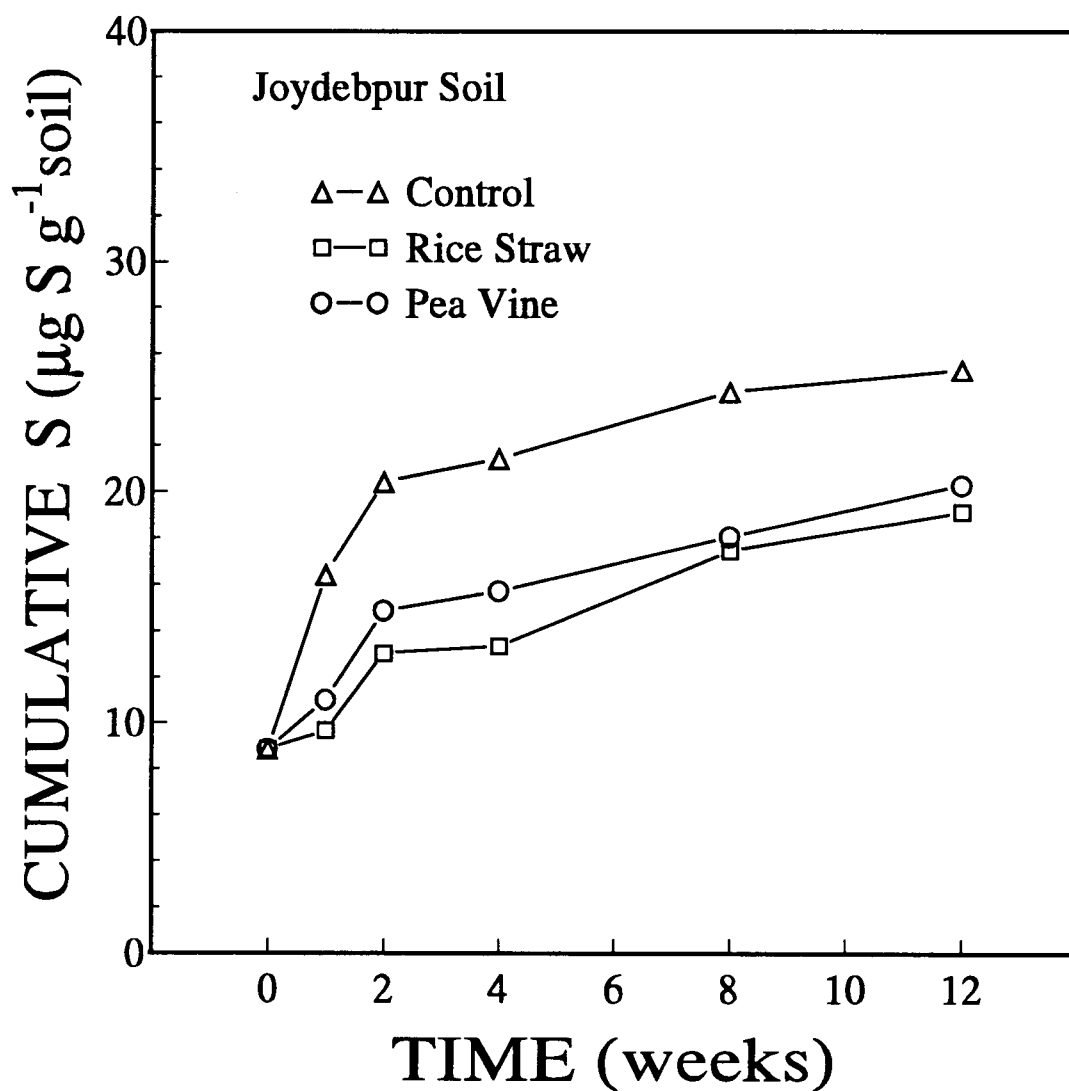


Figure 1.7. Cumulative amount of $\text{SO}_4\text{-S}$ in a Joydebpur soil amended with organic residues under flooded conditions.

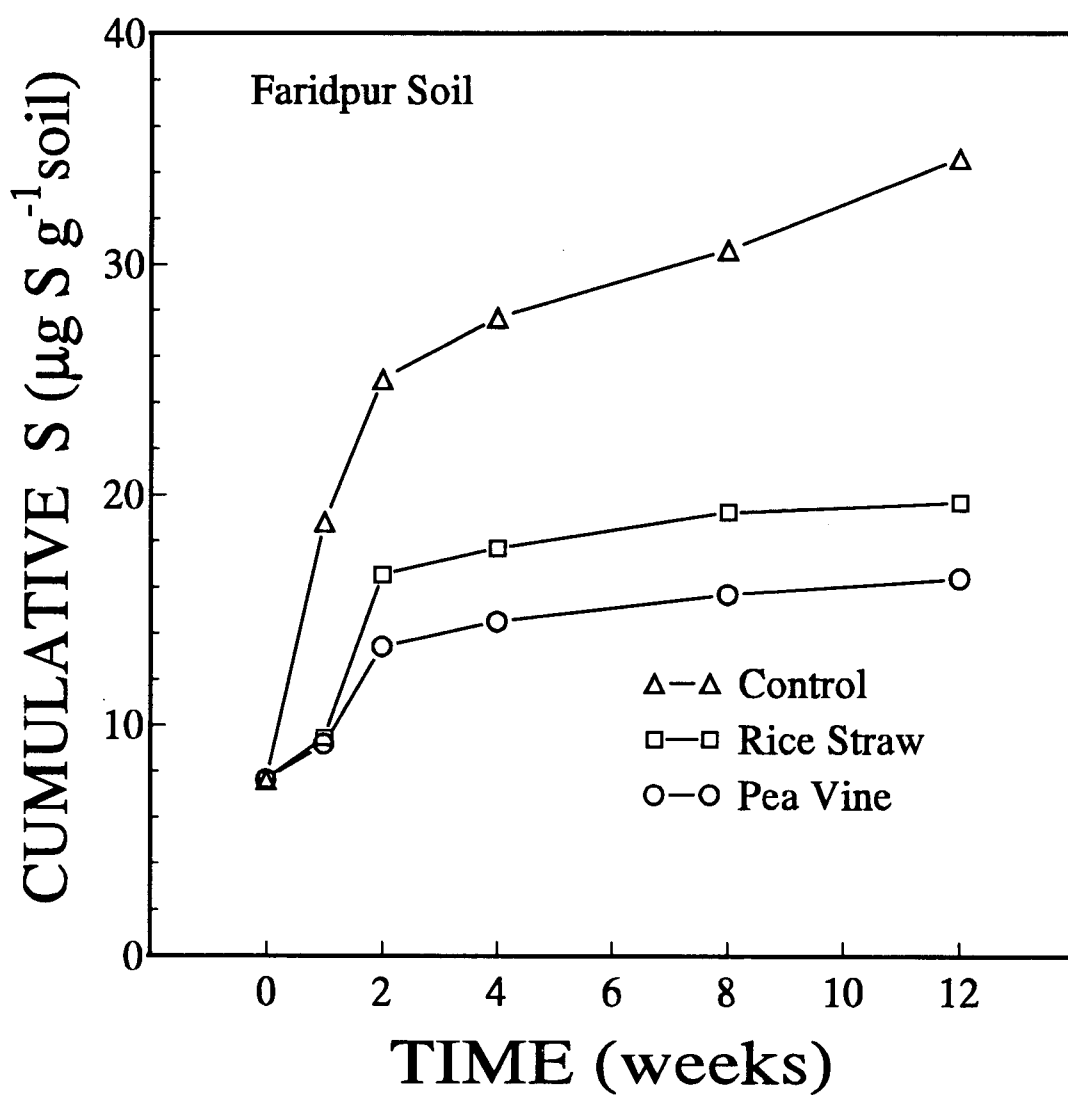


Figure 1.8. Cumulative amount of $\text{SO}_4\text{-S}$ in a Faridpur soil amended with organic residues under flooded conditions.

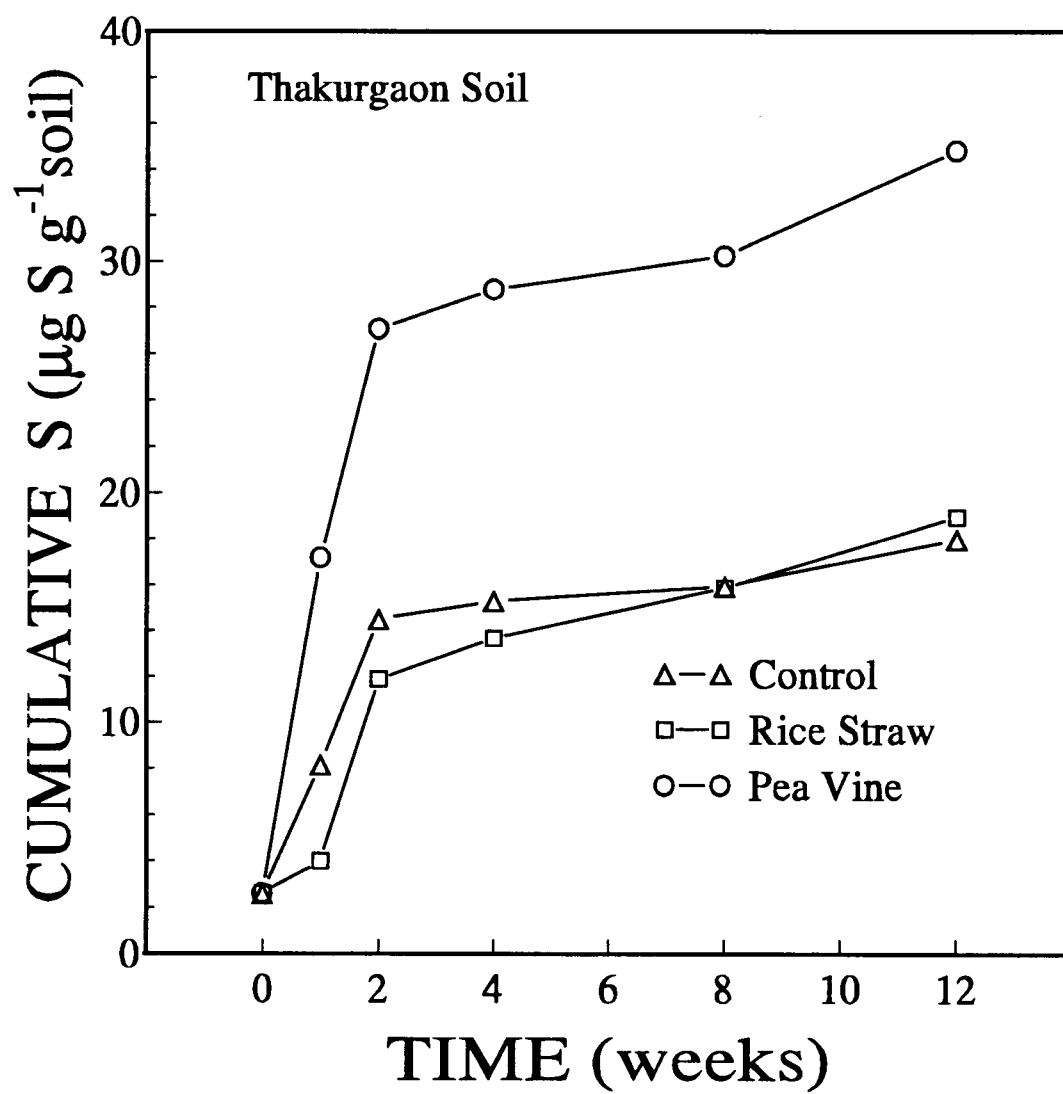


Figure 1.9. Cumulative amount of $\text{SO}_4\text{-S}$ in a Thakurgaon soil amended with organic residues under flooded conditions.

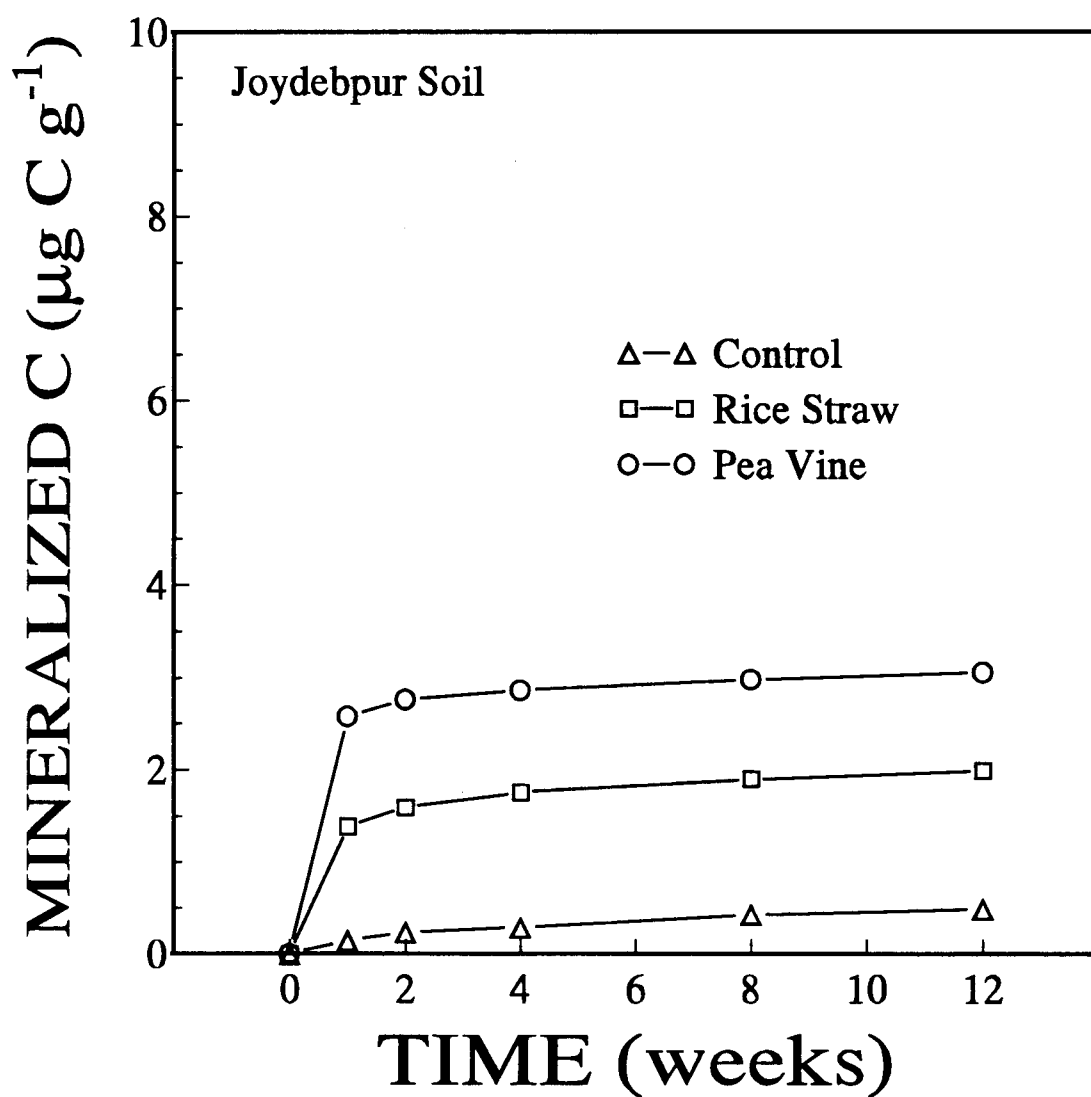


Figure 1.10. Cumulative amount of mineralized C in a Joydebpur soil amended with organic residues under flooded conditions.

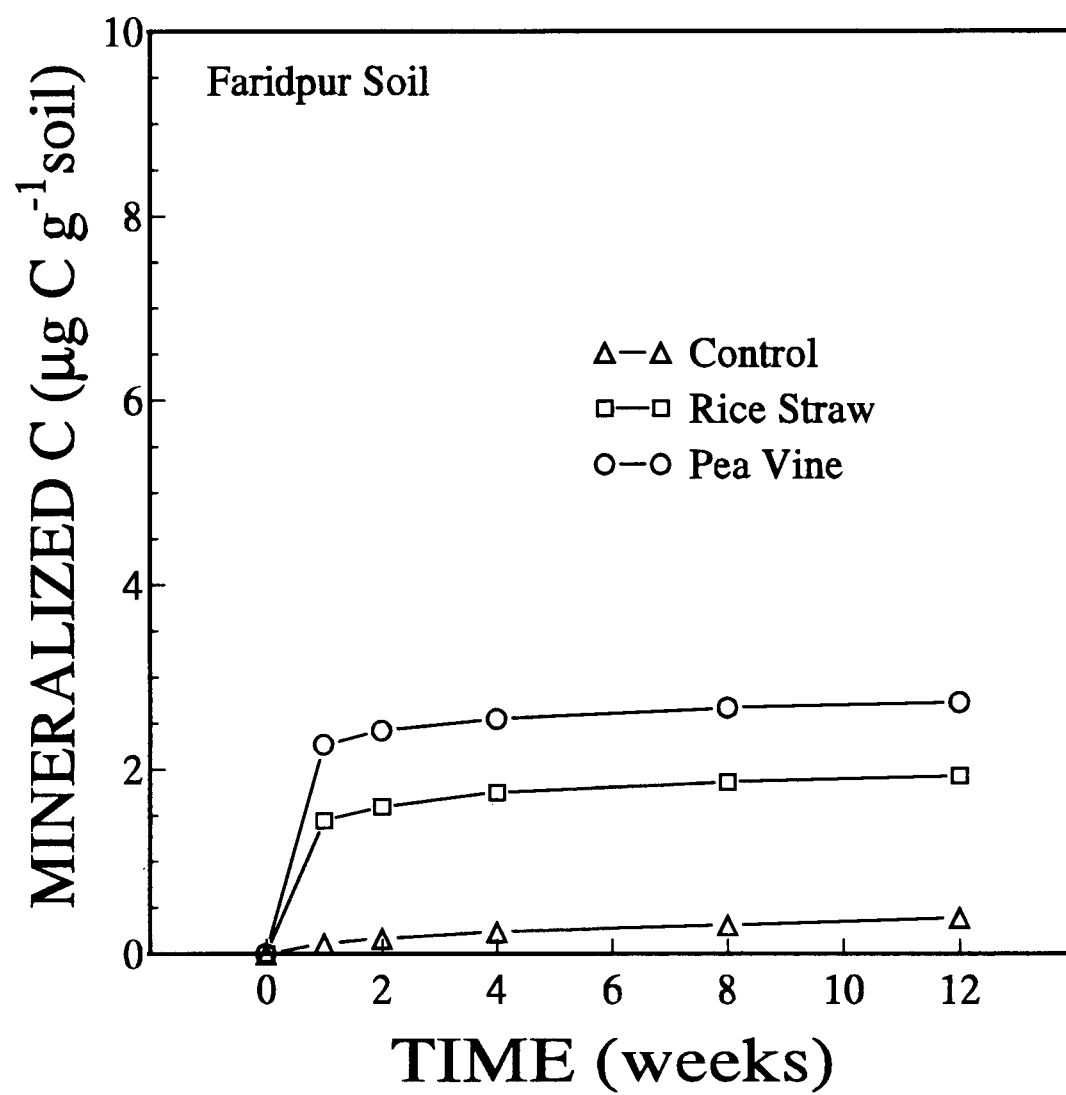


Figure 1.11. Cumulative amount of mineralized C in a Faridpur soil amended with organic residues under flooded conditions.

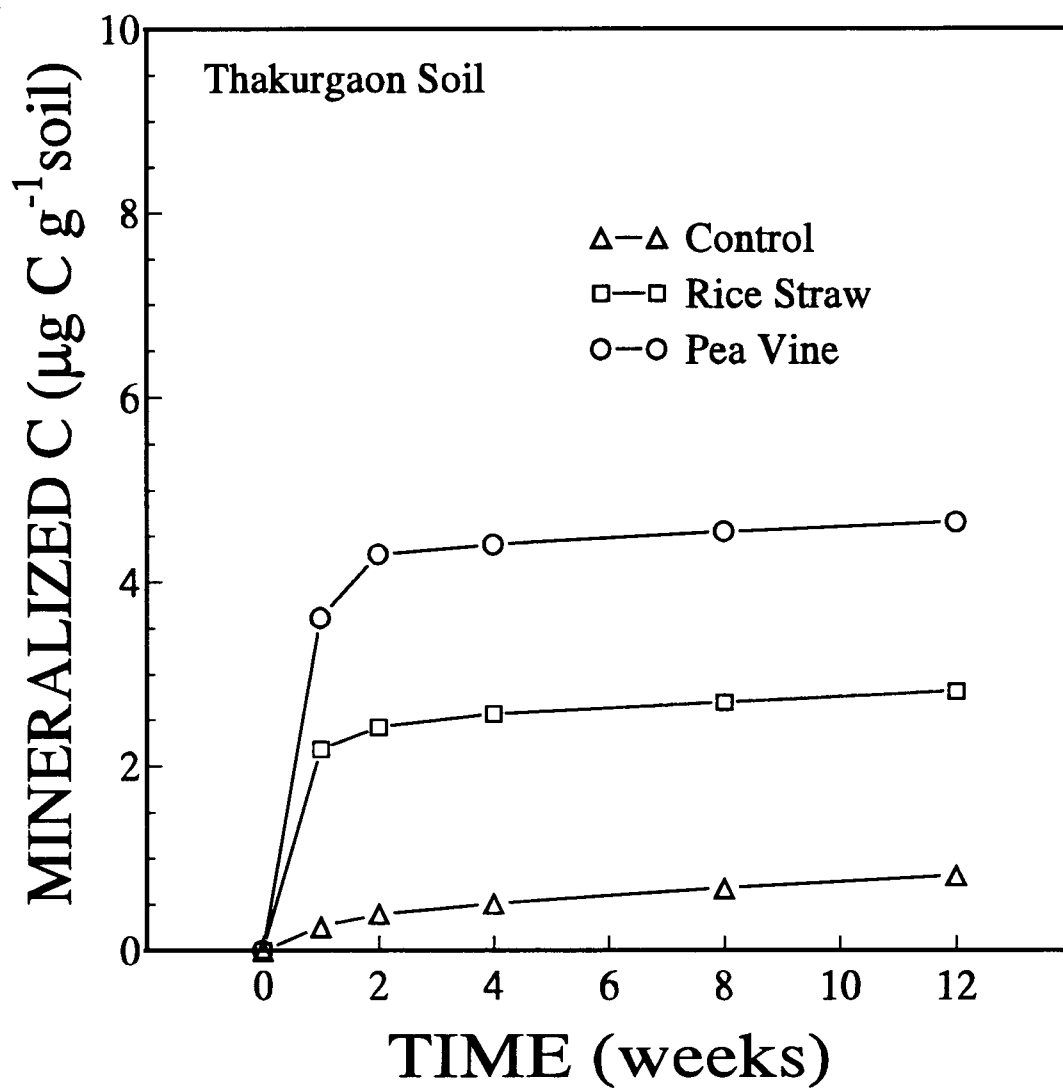


Figure 1.12. Cumulative amount of mineralized C in a Thakurgaon soil amended with organic residues under flooded conditions.

CHAPTER II

EFFECT OF ORGANIC RESIDUE AMENDMENTS ON THE MINERALIZATION OF NITROGEN IN FLOODED RICE SOILS

ABSTRACT

This study was undertaken to assess the mineralization of N in rice soils amended with organic residues under flooded condition. A lab incubation study with a 3 X 3 factorial design (two replications) that had the following treatments: three rice soils, 1) Joydebpur, 2) Faridpur, and 3) Thakurgaon; and three straw amendments added to soils as 1) control, 2) rice straw (*Oryza sativa* L.) or 3) pea vine (*Pisum sativum* L.). The organic residues (25 mg straw g⁻¹ soil) were mixed with soil and glass beads were added (1:1, soil to bed ratio), and transferred into a pyrex leaching tube, flooded and then incubated at 35°C for up to 12 weeks. At 1, 2, 4, 8, and 12 weeks soils in the leaching tubes were leached with deionized water to measure NH₄-N, NO₃-N and other chemical properties of the soil. N mineralization in soils amended with rice straw or pea vine showed a similar N mineralization pattern but rice straw had a higher N mineralization rate than pea vine, which was due to a lower C:N ratio for rice straw. The potentially mineralizable N pool (N₀) and rate constants (K_N) in soils amended with rice straw and pea vine under flooded conditions were estimated using an exponential equation. Rice straw had 7 to 15 times, and pea vine had 3 to 9 times greater N₀ values than the control. The K_N values for unamended soils ranged from 0.35 to 0.52 mg N kg⁻¹ wk⁻¹ and rice straw and pea vine treated soils were from 0.75 to 1.22 and 0.46 to 0.58 mg N kg⁻¹ wk⁻¹. The lower N₀ and K_N values in pea vine treatments suggested there was greater immobilization of N than in rice straw treatments.

INTRODUCTION

Over 90% of the total nitrogen (N) in soils is in organic form. Although atmospheric N can contribute inorganic forms of N to soils, normally the amounts are small compared to crop's requirement. Therefore, organic N must first be mineralized to inorganic forms before it can become available to plants.

Standford and Smith (1972) proposed an incubation leaching technique to study the N mineralization potentials of soils, and found that the cumulative net mineralized N was linearly related to the square root of time ($t^{1/2}$). Using this open incubation leaching technique, Tabatabai and Al-Khafaji (1980) found a linear relationship between the cumulative amount of N and S mineralized with time of incubation. Nitrogen mineralization studies with this approach provide information on the optimal or potential for N mineralization of a soil or soil amendment to provide N to plants.

Nitrogen transformations in flooded soils and sediments are markedly different from those taking place in drained soils. The differences in behavior of N in upland and submerged soils is due largely to the difference in activity of the microorganisms functioning under aerobic or anaerobic conditions. In well drained soil, most N transformations are carried out by aerobic or sometimes facultative anaerobic bacteria, while in submerged soils facultative anaerobic and true anaerobic bacteria predominate.

The major microbial processes involving N in flooded soil are mineralization, immobilization, nitrification, denitrification, and N fixation. A unique

characteristic of flooded soils is that all of these processes can be occurring at the same time because of the presence of both aerobic and anaerobic zones. Thus, a flooded soil is very complex system in relation to N transformations (Patrick, 1982).

However, very little information is available on the N mineralization rates and potentials of wetland rice soils. Therefore, the objective of this study was to assess the effect of added organic residues on the potentially mineralizable N pool and first-order rate constants of some wetland rice soils under flooded conditions.

MATERIALS AND METHODS

The soils used were surface soils (0-15 cm) selected to represent the large rice growing areas of Bangladesh. Sample preparation and chemical and physical analyses were reported in Chapter I.

Incubation procedure

The details of the incubation and analytical procedures were described in Chapter I. The method involved three rice soils (Joydebpur, Faridpur and Thakurgaon) each being amended with one of three organic residue treatments: 1) control, 2) rice straw (*Oryza sativa* L.), or 3) pea vine (*Pisum sativum* L.). Thirty g air-dried soil (2-mm sieved) and an equal weight of glass beads (0.45 to 0.52 mm in diameter) and 0.75 g of each of organic residues (25 mg g⁻¹ soil) were mixed thoroughly and transferred into Pyrex leaching tubes. Soils in the leaching tubes were

flooded by adding 50 ml deionized (DI) water in each leaching tube and incubated at 35°C in an incubator for 12 weeks.

At 1, 2, 4, 8, and 12 weeks the soil:glass beads mixture was leached with 100 or 60 ml (last three sampling periods) DI water in five increments under a vacuum to remove the mineral N produced in the soil. Soil:glass beads mixtures were leached carefully so that soils always remained flooded. The moisture content of the leaching tubes was adjusted by weighing the columns every alternate day and DI water was added as needed.

The leachate was analyzed for NO₃-N by ion chromatography and NH₄-N by steam distillation procedure of Bremner and Keeney (1965). All incubations were carried out in duplicate. The analyses reported are the averages of duplicate determinations.

The exponential equation proposed by Stanford and Smith (1972) was used to measure potentially mineralizable N (N_0) and first-order rate constant (K_N) by the following equation:

$$N_m = N_0[1 - \exp(-K_N t)]$$

where N_m = cumulative amount of inorganic N under flooded incubation at specific time (t).

RESULTS AND DISCUSSION

Mineralization of Nitrogen

The relationship between cumulative inorganic N in soils amended with organic residues is shown in Figures 2.1 to 2.3. Cumulative N mineralization in all three soils amended with rice straw or pea vine showed similar N mineralization patterns. Among the two organic residue sources, rice straw had a higher accumulation of N over pea vine residue. High mineralization of N in soils treated with rice straw was probably due to a lower C:N ratio (14:1) of rice straw than a wider C:N ratio (30:1) of pea vine. In a 12-week decomposition period Barrow (1960) reported that organic matter added to aerobic soils with a C:N ratio of 16 and 44 were the minimum and maximum values respectively, at which no mineralization of N occurred.

Harmsen and Kolenbrander (1965) reported that C:N ratio of the decomposing material must be below 20 to 25 for an appreciable net mineralization. The potentially mineralizable N pool (N_0) and first-order rate constant (K_N) in soils amended with organic residues and incubated under flooded conditions are given in Table 2.1. In calculating the N_0 and K_N values, the initial N values were subtracted from the cumulative N values. The K values for unamended soils ranged from 0.351 to 0.522 mg N kg⁻¹ wk⁻¹, and the soils treated with rice straw and pea vine were from 0.753 to 1.227 and 0.465 to 0.586 mg N kg⁻¹ wk⁻¹, respectively. These rates are much lower than those reported for aerobic soils by Tabatabai and Al-Khafaji (1980). They found a linear relationship between cumulative amount of N

with time of incubation at 35°C with K_N values ranging from 7.7 to 17.0 mg N kg⁻¹ wk⁻¹.

The N_0 values in soils amended with rice straw or pea vine were several times greater than the unamended soils. The N_0 values in soils treated with rice straw or pea vine ranged from 119.69 to 323.39 mg N kg⁻¹ soil. In unamended control N_0 values ranged from 20.09 to 40.43 mg N kg⁻¹ soil. Among the two organic residue treatments, rice straw had the highest N_0 and K_N values which again may be related to its narrow C:N ratio. Higher mineralization of N in rice straw treated soils was in agreement with the result of Norman et al (1990). They found that the lower C:N ratio of the rice straw residue in the soil produced higher N mineralization under flooded condition. Using an exponential equation, Stanford and Smith (1972) reported N_0 values ranging from 20 to over 300 mg N kg⁻¹ air-dried soil and K values of 0.54 mg N kg⁻¹ wk⁻¹. The N_0 values (Table 2.1) were in close agreement with N_0 values reported by Stanford and Smith (1972).

Correlation Among Soil Properties and N Parameters Measured under Flooding

The matrix of correlation coefficients (r) among properties of soils measured over 12 weeks flooding are shown in Tables 2.2 to 2.4. The pH and Eh among the soils over 12 weeks flooding were significantly correlated with each other ($P < 0.001$). This would be expected because it is well established that soil pH moves towards neutrality and Eh goes down with flooding (Ponnamperuma, 1977; Gambrell and Patrick, 1978).

Nitrate and cumulative N in all three soils were significantly correlated with pH and Eh. Soluble organic carbon (SOC) and bicarbonate (HCO_3) content of the soils showed a significant correlation with $\text{NH}_4\text{-N}$ and combined N ($\text{NH}_4 + \text{NO}_3$) content of the soils. In acid rice soil, Patrick and Wyatt (1964) also found higher mineralization of N under waterlogged conditions which they related to an increase in pH with flooding (they showed a change of pH 4.4 to 7.0). The change in pH with flooding may increase mineralization by having a more favorable pH for microbial activity.

CONCLUSIONS

Potentially mineralizable N (N_0) and first-order rate constants (K_N) in soils amended with rice straw and pea vine under flooded conditions were estimated using exponential equation of Standford and Smith (1972). Nitrogen mineralization in soils amended with rice straw or pea vine had similar pattern but rice straw treated soils had higher mineralization rates than pea vine treated soils. The low C:N ratio of rice straw favored N mineralization.

The K_N values for unamended soils ranged from 0.35 to 0.52 $\text{mg N kg}^{-1} \text{wk}^{-1}$ and residue amended soils ranged from 0.465 to 1.227 $\text{mg N kg}^{-1} \text{soil}$. The N_0 values in soils amended with rice straw and pea vine were several times greater than the unamended soils. Rice straw had N_0 values 7 to 15 higher than the control. Among the organic residue treatments, rice straw had the highest N_0 and

K_N values. Low N_0 and K_N values in pea vine treated soils were associated with high C:N ratio (30:1).

Nitrate-N and cumulative N in all three soils were significantly correlated with pH and Eh of the soils with time of incubation. Soluble organic carbon (SOC) and bicarbonate (HCO_3) content of the soils showed significant correlation with NH_4 -N and combined N ($NH_4 + NO_3$) contents of the soils.

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Table 2.1. Nitrogen mineralization constants[†] for soils amended with organic residues and incubated under continuous flooding condition.

Residue Treatments	N ₀	K _N	R ² [‡]
<u>Joydebpur Soil</u>			
Control	40.43	0.522	0.92
Rice straw	283.24	0.753	0.96
Pea vine	124.06	0.465	0.99
<u>Faridpur Soil</u>			
Control	20.09	0.516	0.99
Rice straw	298.88	0.873	0.97
Pea vine	119.69	0.491	0.90
<u>Thakurgaon Soil</u>			
Control	35.82	0.351	0.94
Rice straw	323.39	1.227	0.97
Pea vine	144.40	0.586	0.98

[†]N₀ = potential mineralizable N (mg N kg⁻¹ soil) and K_N = first-order rate constant (mg N kg⁻¹ wk⁻¹).

[‡]Significant at P < 0.05.

Table 2.2. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Joydebpur soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	NH ₄ -N	NO ₃ -N	Com N [§]	Cum N [¶]
pH	--	-0.95***	0.09	0.21	0.01	-0.95***	-0.04	0.47**
Eh		--	-0.19	-0.39*	-0.19	0.92***	-0.14	-0.46**
SOC			--	0.74***	0.54***	-0.08	0.54***	-0.02
HCO ₃				--	0.89***	-0.27	0.88***	0.21
NH ₄ -N					--	-0.03	0.99***	0.30
NO ₃ -N						--	0.02	-0.49**
Com N							--	0.27
Cum N								--

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]Com N = combined flood water and soil extractable at each sampling time increment N (NH₄ + NO₃).

[¶]Cum N = cumulative N. Summation of floodwater and soil extractable N up to each sampling time increment.

Table 2.3. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Faridpur soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	NH ₄ -N	NO ₃ -N	Com N [§]	Cum N [¶]
pH	--	0.86 ^{***}	-0.15	-0.19	-0.04	0.88 ^{***}	0.24	-0.56 ^{***}
Eh		--	-0.18	-0.31	-0.19	0.99 ^{***}	0.12	-0.48 ^{**}
SOC			--	0.85 ^{***}	0.58 ^{***}	-0.22	0.52 ^{**}	0.02
HCO ₃				--	0.88 ^{***}	-0.33 [*]	0.78 ^{***}	0.22
NH ₄ -N					--	-0.18	0.95 ^{***}	0.34 [*]
NO ₃ -N						--	0.14	-0.43 ^{**}
Com N							--	0.21
Cum N								--

^{***},^{**},^{*}Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]Com N = combined flood water and soil extractable at each sampling time increment N (NH₄ + NO₃).

[¶]Cum N = cumulative N. Summation of floodwater and soil extractable N up to each sampling time increment.

Table 2.4. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Thakurgaon soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	NH ₄ -N	NO ₃ -N	Com N [§]	Cum N [¶]
pH	--	-0.93***	0.11	0.29	0.13	-0.94***	0.10	0.51**
Eh		--	-0.04	-0.28	-0.12	0.90**	-0.09	-0.41*
SOC			--	0.57***	0.61***	-0.17	0.60***	0.03
HCO ₃				--	0.94***	-0.26	0.93***	0.39*
NH ₄ -N					--	-0.04	0.99***	0.30
NO ₃ -N						--	-0.01	-0.43**
Com N							--	0.29
Cum N								--

***, ** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]Com N = combined flood water and soil extractable at each sampling time increment N (NH₄ + NO₃).

[¶]Cum N = cumulative N. Summation of floodwater and soil extractable N up to each sampling time increment.

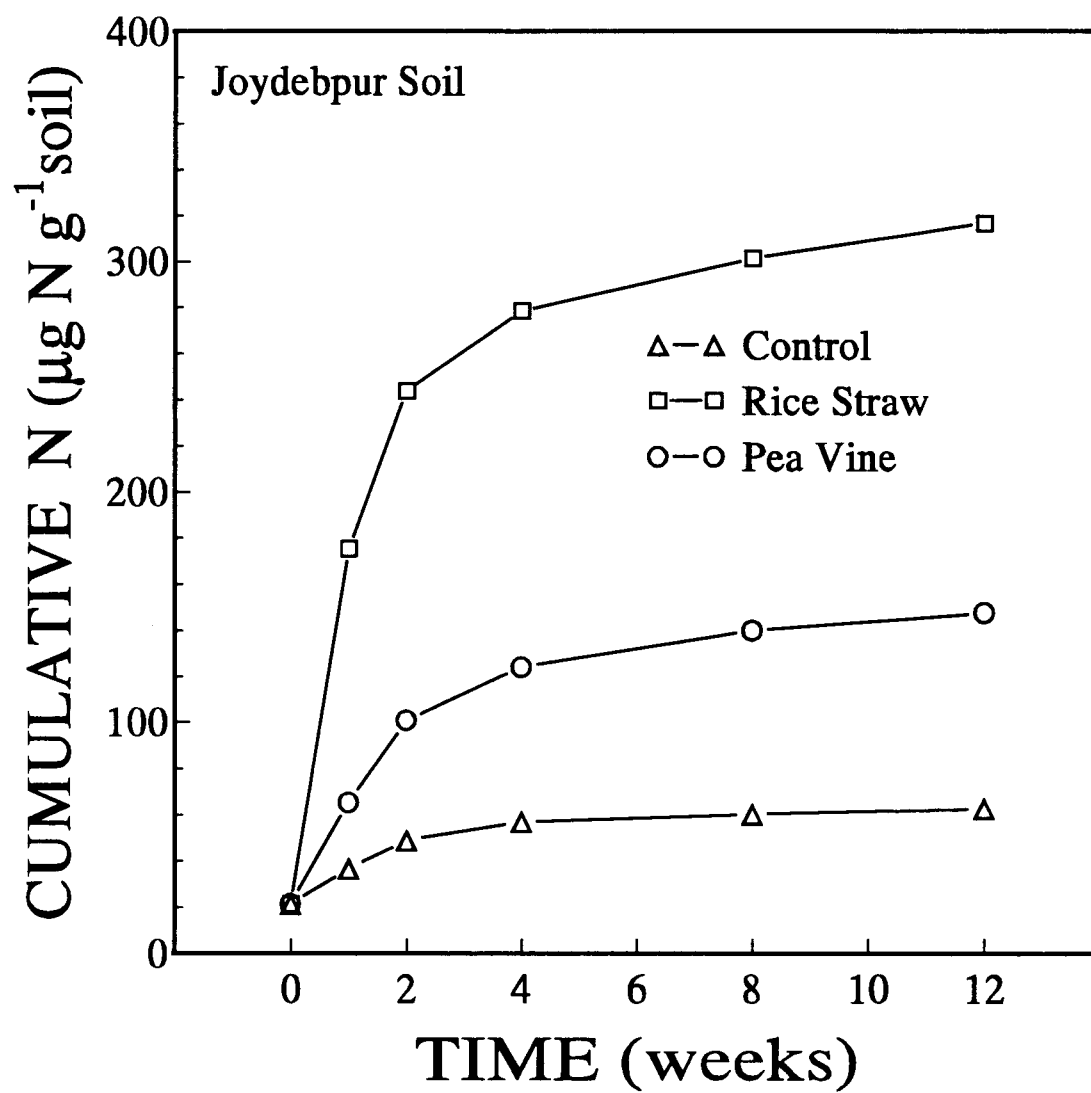


Figure 2.1. Cumulative amount of inorganic N ($\text{NO}_3+\text{NH}_4\text{-N}$) in a Joydebpur soil amended with organic residues under flooded conditions.

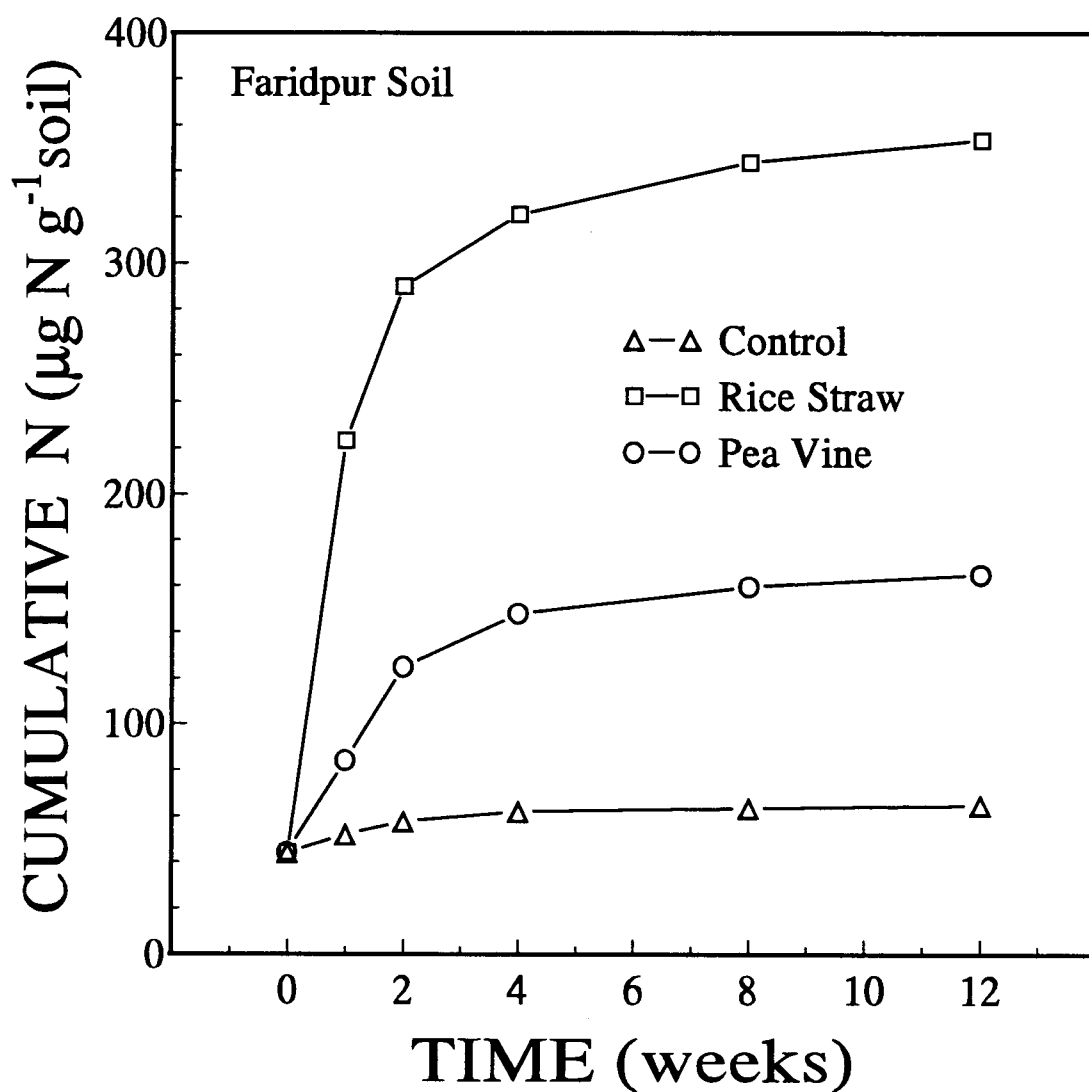


Figure 2.2. Cumulative amount of inorganic N ($\text{NO}_3+\text{NH}_4\text{-N}$) in a Faridpur soil amended with organic residues under flooded conditions.

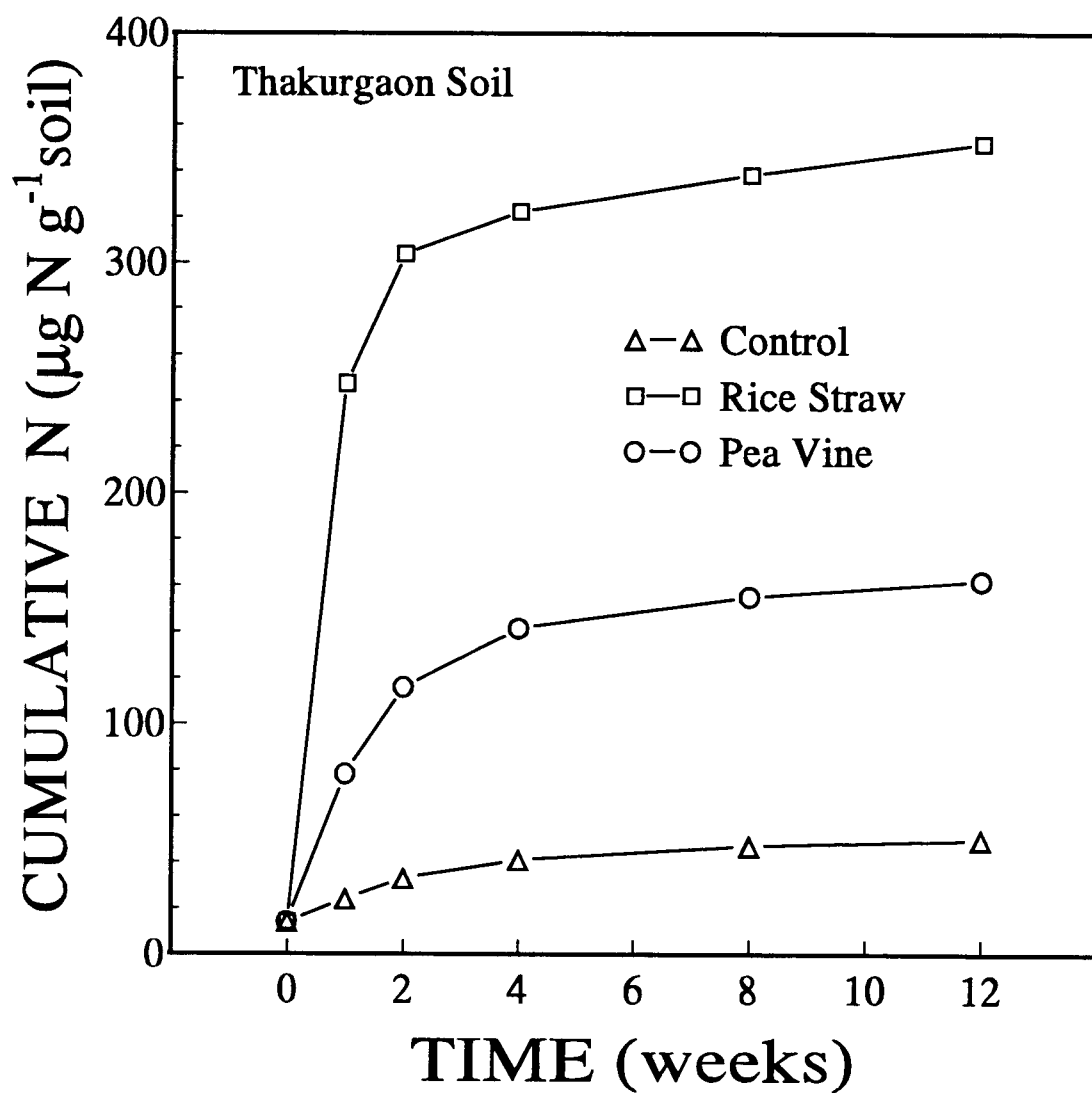


Figure 2.3. Cumulative amount of inorganic N ($\text{NO}_3+\text{NH}_4\text{-N}$) in a Thakurgaon soil amended with organic residues under flooded conditions.

CHAPTER III

EFFECT OF ORGANIC RESIDUE AMENDMENTS ON THE RELEASE OF PHOSPHORUS IN FLOODED RICE SOILS

ABSTRACT

This study was undertaken to assess the $\text{PO}_4\text{-P}$ released in rice soils amended with organic residues under flooded conditions. A lab incubation study was conducted with a 3 X 3 factorial design (two replications) that had the following treatment: three rice soils (Joydebpur, Faridpur, and Thakurgaon); and three organic residue soil amendments [control, rice straw (*Oryza sativa* L.), and pea vine (*Pisum sativum* L.)]. The organic residues (25 mg g^{-1} soil) were mixed with soil and glass beads added (1:1, soil to bed ratio) and transferred into a leaching tube. Soils were kept flooded and incubated at 35°C for up to 12 weeks. At 1, 2, 4, 8, and 12 weeks soils in the leaching tubes were leached with deionized water and analyzed for $\text{PO}_4\text{-P}$ and other chemical properties of the soils. Cumulative $\text{PO}_4\text{-P}$ released in all three soils treated with rice straw showed a significantly higher release of P over pea vine or control treatments. Low $\text{PO}_4\text{-P}$ released in pea vine treated soils suggests immobilization of P due to wide C:P ratio (252:1) of pea vine. The amount of $\text{PO}_4\text{-P}$ released under flooded condition depends on: soil type, C:P ratio of organic residues, and incubation time. $\text{PO}_4\text{-P}$ and cumulative P in all three soils were significantly correlated to pH and Eh.

INTRODUCTION

Phosphorus (P) is an essential plant nutrient and is often deficient in crop production. Phosphorus content of soil may vary from 0.02 to 0.5% with an average value of approximately 0.05% (Barbar, 1984). Phosphorus in soil may be present in four major categories: 1) soluble form in soil solution; 2) absorbed on the surfaces of inorganic soil constituents; 3) P minerals, both crystalline and amorphous; and 4) as a component of soil organic matter. Among the different categories, large fractions of P are present in a mineral form which are not readily available to plant uptake (Barbar, 1984).

One-half or more of the total P in the A horizon of soils may be present as organic P. The release of organic P into the soil solution for plant absorption is controlled by the rate of organic matter mineralization. In temperate climate soils the rate of mineralization of organic matter depends on soil texture and environmental conditions. Averaged over 10 years, Larson et al. (1972) reported that 1.9% of the total P was mineralized each year in Iowa.

The greatest effects of organic P have been observed in the tropics (Anderson, 1980), where organic P can apparently supply a large part of the crop P requirement. In tropical soils, where temperatures are high, organic matter decomposition is rapid and thus supplies more P than does organic matter in temperate soils.

Upon flooding the availability of P to plants increases. In acid soils the increase in P availability is associated with a decrease in Eh or increase in iron

(Fe²⁺) (Ponnamperuma, 1965; Patrick and Mahapatra, 1968). In alkaline soils the increase in solubility of P is a consequence of the decrease in pH of these soils on flooding, for the solubility of hydroxylapatite increases as pH decreases (Stumm and Morgan, 1970). But the phosphate ions released by these reactions and from the decomposition of organic matter may be resorbed by clay and hydrous oxides of Al in the anaerobic zone (Bromfield, 1960) or they may diffuse to oxidized zones and be reprecipitated.

In submerged soils up to 60% of the water-soluble P may be in organic form (Ponnamperuma, 1972) indicating the importance of organic matter decomposition in the bioavailability of P to wetland rice. Little is known about the P release pattern in flooded rice soils. Therefore, this study was undertaken to assess the effect of added organic residues on the P release in wetland rice soils under flooded conditions.

MATERIALS AND METHODS

The soils used were surface soils (0-15 cm) selected to represent the large rice growing areas of Bangladesh. Sample preparation and chemical and physical analyses of the soils are reported in Chapter I.

Incubation procedure

The details of the incubation and analytical procedures were described in Chapter I. A lab incubation study was conducted with a 3 X 3 factorial design

(two replications) that had the following treatment: three rice soils (Joydebpur, Faridpur, and Thakurgaon); and three organic residue soil amendments [control, rice straw (*Oryza sativa* L.), and pea vine (*Pisum sativum* L.)]. Organic residues were applied at the rate of 25 mg g⁻¹ soil. Thirty g air-dried soil (2 mm sieved) and an equal weight of glass beads (0.45 to 0.52 mm diameter) were mixed thoroughly with organic residues and transferred into Pyrex leaching tubes. Soils in the leaching tubes were incubated at 35°C and were kept flooded by adding 50 ml deionized (DI) water in each leaching tube.

During sampling time the soil:glass beads mixtures were leached with 100 ml DI water in five increments to remove the available PO₄ released in to the soil solution. The leaching procedure was done at 1, 2, 4, 8, and 12 weeks. The moisture content of the leaching tubes was adjusted by weighing the columns every alternate day by adding DI water as needed. At 4, 8, and 12 weeks 60 ml leachate were collected.

Leachate obtained was analyzed for PO₄-P using a Dionex ion chromatograph. All incubations were carried out in duplicate and results are reported as the mean of two replication on a soil dry weight basis.

RESULTS AND DISCUSSION

The relationship between cumulative PO₄ released in soils treated with organic residues under flooded condition is shown in Figures 3.1 to 3.3. All three soils treated with rice straw showed a significantly higher release of PO₄ over pea

vine or control treatments. Pea vine treatment failed to produce more PO_4 over control treatment. The low amount of PO_4 released in pea vine treated soils was probably due to wide C:P ratio of pea vine (252:1 vs 55:1 for rice straw).

Phosphate-P released in soils amended with organic residues under flooded condition showed a pattern of little initial release of $\text{PO}_4\text{-P}$ followed by gradual linear release up to 12 weeks. Low initial release of $\text{PO}_4\text{-P}$ in soil was probably due to microbial immobilization of P. Later linear release of $\text{PO}_4\text{-P}$ in acid soils have usually been attributed to the reduction of ferric phosphate (Patrick and Mahapatra, 1968) and increased solubility of CaP compounds in alkaline soils due to flooding. Organic acid complexes of Fe^{2+} , Fe^{3+} and Al^{3+} would be expected to increase dissolution of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$. Martell et al (1988) reported that organic acids such as oxalate can increase the solubility of both P and Al in soils through the formation of stable complexes with Al. Legand-exchange reactions between oxalate and P at oxide surfaces directly release P to solution (Stumm, 1986). The cumulative values of water soluble Fe^{2+} and Mn^{2+} in organic residue treated soils were higher compared to control treatment (Chapter I, Tables. 1.3 and 1.4). The PO_4 released in alkaline Faridpur soil was assumed to be due to increased solubility of CaP compounds due to flooding.

It is evident from the result that the amount of $\text{PO}_4\text{-P}$ released in soils under flooded conditions depends on: C:P ratio and nature of organic residues, soil type and time of incubation.

The matrix of correlation coefficients (r) among properties of soils measured over 12 weeks flooding incubation are shown in Tables 3.1 to 3.3. Phosphate-P,

and cumulative P in all three soils were significantly correlated with soil pH and Eh. Among the three soils, PO_4 and cumulative P in Joydebpur soil showed a significant correlation with cumulative iron (Fe^{2+}) and manganese (Mn^{2+}) content of the soil. The results obtained were in agreement with the reports of Ponnampetuma (1965) and Patrick and Mahapatra (1968) that the availability of P in acid soil increases due to decrease in Eh and increase in pH of the soil. Conversely, P availability in alkaline soils increases with decrease in pH (Stumm and Morgan, 1970), and Eh due to flooding. The increased release in PO_4 is due to solubility of inorganic P compounds (Fe and Al compounds in acid soils and CaP compounds in alkaline soils) and increased microbial activity with development of a more favorable pH (neutral) under flooding conditions.

CONCLUSIONS

Cumulative PO_4 -P release under flooding conditions in all three soils treated with rice straw showed a significantly higher release of PO_4 -P over pea vine or control treatments. Lower P release in the pea vine residue suggested immobilization of P was occurring which was probably due to wide C:P ratio (252:1) of the pea vine. Higher PO_4 release in flooded soils amended with organic residues there were increased levels of soluble Fe and Mn over the control. This indicates that organic amendments promote the release of PO_4 from precipitated PO_4 compounds associated with Fe and Mn. Since C:P ratio of added organic residues also was important, the results suggest that organic residues promote both chemical release

of PO_4 and biological mineralization of organic P. Among the various soil properties, PO_4 -P levels and cumulative P in all three soils were significantly correlated to pH and Eh of the soils with time of flooding.

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Table 3.1. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Joydebpur soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	PO ₄ -P	Cum PO ₄ -P [§]	Cum Fe [¶]	Cum Mn [#]
pH	--	-0.95***	0.09	0.21	0.47**	0.46**	0.48**	0.53***
Eh		--	-0.19	-0.39*	-0.40*	-0.38*	-0.47**	-0.43**
SOC			--	0.74***	-0.30	-0.26	0.05	0.10
HCO ₃				--	-0.22	-0.31	0.28	0.21
PO ₄ -P					--	0.89***	0.72***	0.43**
Cum PO ₄ -P						--	0.68***	0.38*
Cum Fe							--	0.76***
Cum Mn								--

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]Cum PO₄-P = cumulative PO₄-P at each sampling time increment.

[¶]Cum Fe = cumulative iron (Fe²⁺).

[#]Cum Mn = cumulative manganese (Mn²⁺).

Table 3.2. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Faridpur soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	PO ₄ -P	Cum PO ₄ -P [§]	Cum Fe [¶]	Cum Mn [#]
pH	--	0.86***	-0.15	-0.19	0.50**	-0.53***	-0.61***	-0.69***
Eh		--	-0.18	-0.31	-0.43**	-0.41*	-0.43**	-0.53***
SOC			--	0.85***	-0.13	-0.19	0.21	0.13
HCO ₃				--	0.07	-0.15	0.22	0.30
PO ₄ -P					--	0.77***	0.13	0.70***
Cum PO ₄ -P						--	0.17	0.69***
Cum Fe							--	0.69***
Cum Mn								--

*, **, *** Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]Cum PO₄-P = cumulative PO₄-P at each sampling time increment.

[¶]Cum Fe = cumulative iron (Fe²⁺).

[#]Cum Mn = cumulative manganese (Mn²⁺).

Table 3.3. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation of a Thakurgaon soil under flooded condition.

Properties	pH	Eh	SOC [‡]	HCO ₃	PO ₄ -P	Cum PO ₄ -P [§]	Cum Fe [¶]	Cum Mn [#]
pH	--	-0.93***	0.11	0.29	0.35*	0.39*	0.51**	0.46**
Eh		--	-0.04	-0.28	-0.38*	-0.37*	-0.27	0.21
SOC			--	0.57**	-0.08	-0.17	0.05	0.25
HCO ₃				--	0.39*	0.01	0.04	0.11
PO ₄ -P					--	0.75***	-0.03	-0.09
Cum PO ₄ -P						--	0.07	0.01
Cum Fe							--	0.93***
Cum Mn								--

*, **, ***Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 36.

[‡]SOC = soluble organic carbon.

[§]Cum PO₄-P = cumulative PO₄-P at each sampling time increment.

[¶]Cum Fe = cumulative iron (Fe²⁺).

[#]Cum Mn = cumulative manganese (Mn²⁺).

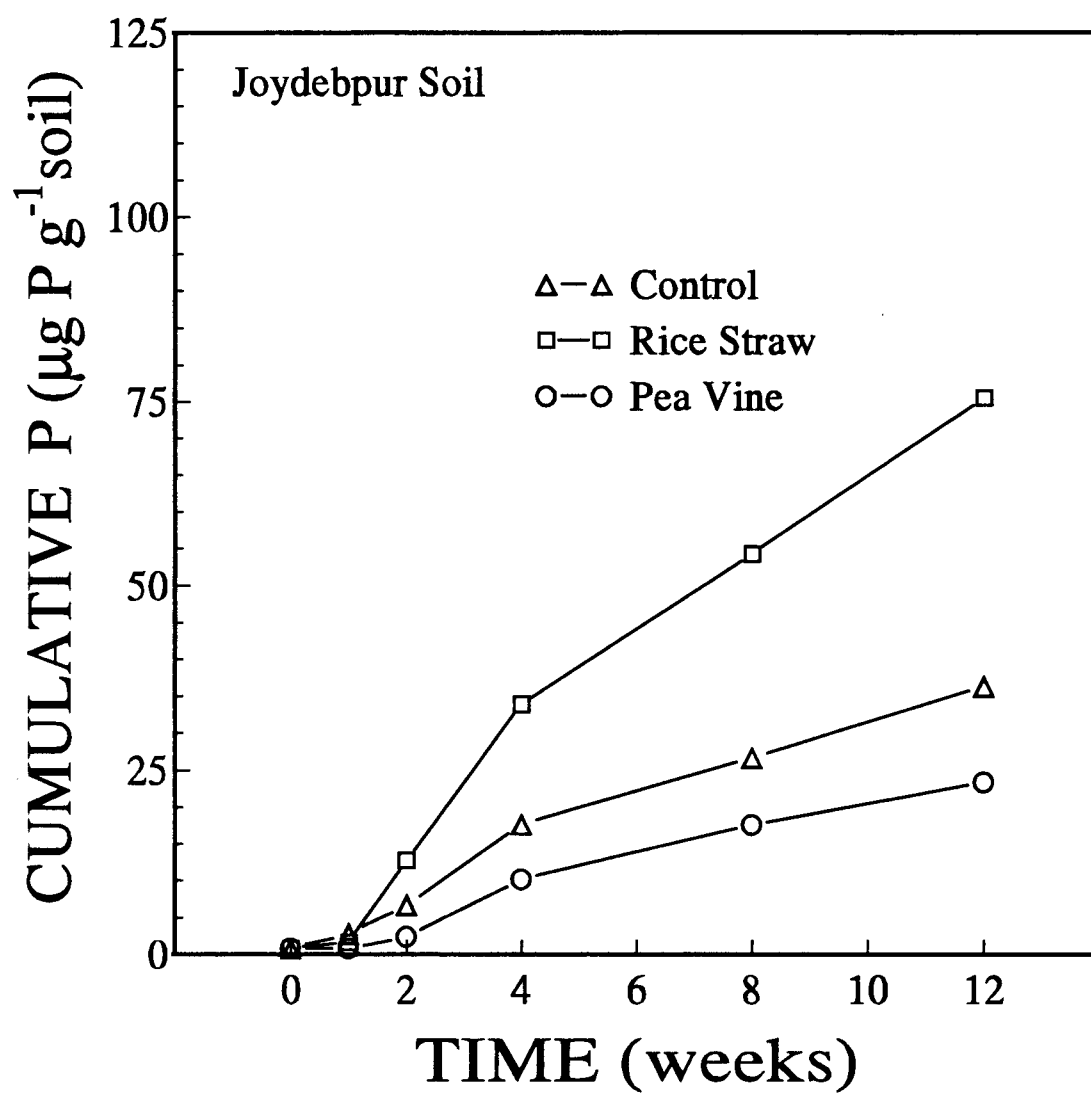


Figure 3.1. Cumulative amount of $\text{PO}_4\text{-P}$ released in a Joydebpur soil amended with organic residues under flooded conditions.

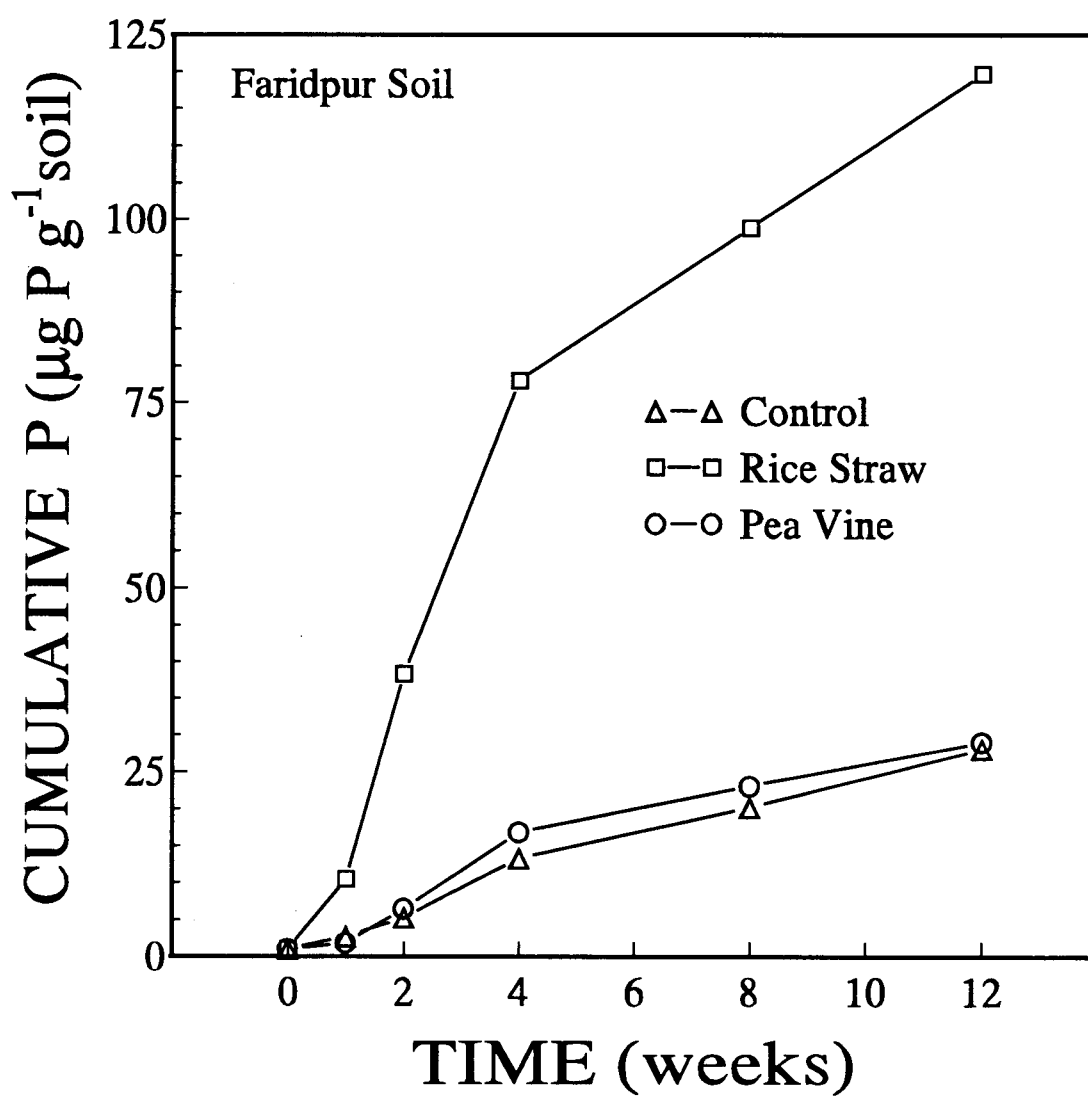


Figure 3.2. Cumulative amount of $\text{PO}_4\text{-P}$ released in a Faridpur soil amended with organic residues under flooded conditions.

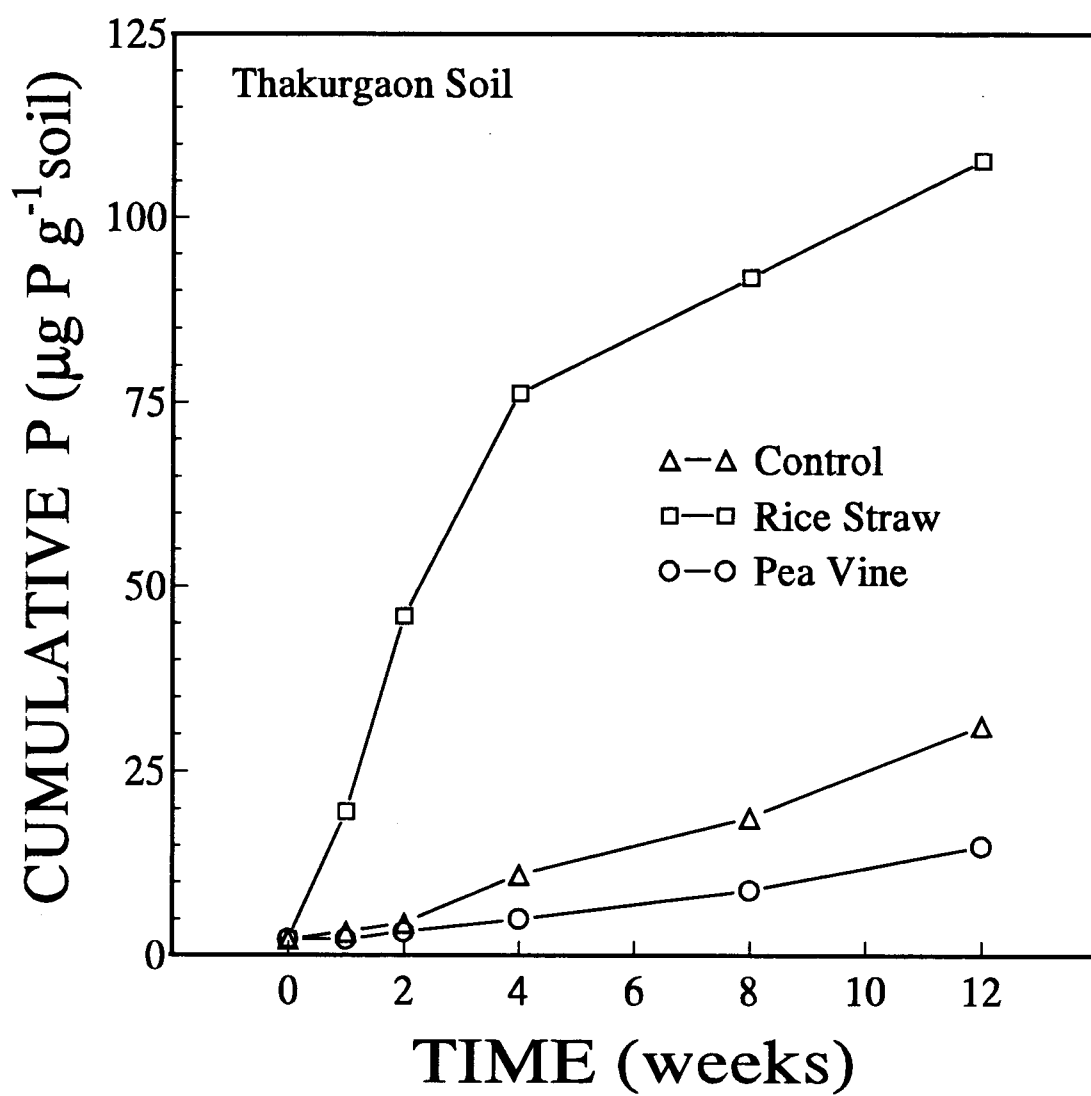


Figure 3.3. Cumulative amount of $\text{PO}_4\text{-P}$ released in a Thakurgaon soil amended with organic residues under flooded conditions.

CHAPTER IV

EFFECT OF RESIDUE C:S RATIO ON THE MINERALIZATION OF SULFUR IN SOILS UNDER AEROBIC-FLOODING CYCLES

ABSTRACT

This study was undertaken to assess the effect of organic residue C:S ratio on the mineralization of S in rice soils under aerobic-flooding cycles. A lab incubation study with a 3 x 2 x 2 factorial design (two replications) was conducted with the following treatments: two rice soils (Faridpur and Joydebpur); three levels of wheat (*Triticum aestivum* L.) straw to soils as control, or straw with C:S ratios of 400:1 or 100:1; and two moisture levels (two week aerobic - flooding cycles or four weeks aerobic - flooding cycles). The organic residues (25 mg straw g⁻¹ soil) were mixed with 30 g soil and glass beads were added in 1:1 ratio with soil and incubated at 35°C. Soils were kept aerobic (75% of field moist) or flooded by adding 50 ml deionized (DI) water in each leaching tube. Soils were leached with DI water and analyzed for SO₄-S and other chemical properties at two week intervals up to 12 weeks. Cumulative SO₄-S in all soils amended with a narrow C:S ratio (100:1) of the straw had a significantly higher accumulation of SO₄-S over the control or wider C:S ratio (400:1). The potentially mineralizable S pool (S₀) and first-order rate constants (K_s) in soils amended with wheat straw under aerobic-flooding cycles were estimated using an exponential equation of Stanford and Smith (1972). The K_s values for unamended soils ranged from 0.112 to 0.160 mg S kg⁻¹ wk⁻¹. The K_s value for straw treated soils ranged from 0.030 to 0.149 mg S kg⁻¹ wk⁻¹. Among the two straw C:S ratio treatments, narrow C:S ratio had the highest K_s values, indicating more microbial mineralization of S. Among the two C:S ratios of the straw treatments, the S₀ value was 1.5 to 2 times more for

narrow C:S ratio (100:1) than wide C:S ratio (400:1) treated soils which implies that narrow C:S ratio of straw residues has potentiality to provide more plant available S in the soil. The cumulative amount of C mineralized was linearly related to time of incubation. The slopes of the regression equation (rate of C mineralization) in unamended soils ranged from 0.014 to 0.019 mg C kg⁻¹ wk⁻¹. Conversely, in the straw amended soils the slopes ranged from 0.027 to 0.042 mg C kg⁻¹ wk⁻¹. Compared to control, the C mineralization rates were 2 to 3 times more in straw treatments in two or four weeks flooding cycles.

INTRODUCTION

Sulfur (S) is an essential nutrient for plant growth. Plants acquire S primarily through the assimilation of sulfate from the soil. In agricultural soils, S is present in both inorganic and organic forms. Among the two forms of S in soils, organic S occupies more than 95% of the total S content of the soils (Tabatabai and Bremner, 1972; Tabatabai, 1984). If S is to be used up by plants, the organic forms of S must be mineralized by soil organisms (Brady, 1974; Williams, 1975).

Sulfur mineralization in soils is biological in nature, and the amount of S mineralized in aerobic soils depends on: soil physical and chemical properties (Pirela and Tabatabai, 1988); types of organic residues (Tabatabai and Chae, 1991); and moisture, aeration, temperature and soil pH (Brady, 1974). Conversely, immobilization of inorganic forms of S occurs when low S-rich organic materials are added to soils not adequately supplied with inorganic S (Barrow, 1960).

The soil is flooded for part or all of the growing season in most of the rice-growing areas of the world. Thus, submerged soil creates conditions markedly different from those of a well drained soil (Patrick and Mahapatra, 1968), which in turn affects S transformations (Freney and Boonjawat, 1983). Due to uncertainties of natural rainfall and management practices, rice soils are often subjected to alternate flooding and drying cycles (Patrick and Mahapatra, 1968). Although there is evidence that rewetting an air-dry soil but under aerobic condition increases S mineralization (Williams, 1967), there is relatively little information on S mineralization rates during transitions from aerobic to flooded conditions and vice versa (Freney, 1986). Therefore, understanding the processes of S mineralization under flooded as well as under alternate wetting and drying cycle is important with respect to S availability to rice plants.

The objective of this study was to determine the effect of residue C:S ratio on the potentially mineralizable S pool and first-order rate constants in rice soils under aerobic-flooding cycles.

MATERIALS AND METHODS

The soils used were surface soils (0-15 cm) selected to represent the large rice growing area of Bangladesh. Sample preparation and chemical and physical analysis of the soils were reported in Chapter I. Chemical analyses of the wheat straw used in the incubation study are shown in Table 4.1, details of the analytical procedures were reported in Chapter I.

Incubation Procedure

Details of the incubation procedure were reported in Chapter I. In brief, a lab incubation study with a 3 x 2 x 2 factorial design (two replications) was carried out for 12 weeks. The treatments were: two rice soils 1) Faridpur, and 2) Joydebpur; three levels of wheat (*Triticum aestivum* L.) straw amended soil, 1) control, 2) straw with C:S ratio of 400:1 or 3) straw with C:S ratio of 100:1; and two moisture levels, 1) two weeks aerobic (75% of field capacity) - flooding cycles, or 2) four weeks aerobic (75% of field capacity)-flooding cycles. Organic residues were applied at the rate of 25 mg g⁻¹ soil.

Thirty g air-dried soil and an equal weight of glass beads (0.45 to 0.52 mm diameter) were mixed and transferred into Pyrex leaching tubes. Soils in the leaching tubes were incubated at 35°C in an incubator as aerobic (75% of field capacity) or flooded by adding 50 mL deionized (DI) water in each leaching tube. The desired C:S ratio of the wheat straw was obtained by growing Stephen wheat in the greenhouse under varying levels of S.

To determine the SO₄ produced, soil-glass beads mixture (1:1) were leached with 60 mL DI water in six increments at two weeks intervals for 12 weeks. The moisture content of the leaching tubes was adjusted by weighing the columns every alternate day and adding DI water as needed. All incubations were carried out in duplicate. The leachate was analyzed for SO₄-S by a Dionex ion chromatograph; total soluble C (TSC) and soluble organic C (SOC) in the leachate was measured on a Dohrman carbon analyzer. The bicarbonate (HCO₃) content was calculated by subtracting SOC values from the TSC values. Water soluble Fe²⁺ was measured by

atomic absorption. The pH and Eh of the soils were measured directly in the incubation tube during the flooding periods using combination glass electrode and combination platinum electrode, respectively.

The exponential equation proposed by Stanford and Smith (1972) was used to measure potentially mineralizable S pool (S_0) and first-order rate constant (K_s) by the following equation:

$$S_m = S_0[1 - \exp(-K_s t)]$$

where S_m = amount of S mineralized under aerobic-flooding incubation at specific time (t). Potentially mineralizable C pool (C_0) and first-order rate constant (K_c) were also estimated by using the same exponential equation.

RESULTS AND DISCUSSION

pH and Eh

The pH of the Faridpur soil (Table 4.2) decreased from a pH of 8.17 to an average pH value of 7.78 at two weeks flooding after following a two weeks or four weeks aerobic incubation; four weeks continuous flooding brought down pH values of the soil a little more with an average value of about 7.49. Conversely, in Joydebpur soil (acid soil) the pH values increased. The pH values attained after two weeks flooding ranges from 7.0 to 7.38 (Table 4.3). The addition of organic residues had no significant effect in increasing or decreasing the pH of the soils.

Field moist condition followed by two weeks flooding markedly decreased the Eh of the soils. In Faridpur soil the Eh value dropped down from +142 mV (at

0 week) to an average (across C:S treatments) value of +105 mV after two weeks aerobic flooding and +93 mV at four weeks aerobic flooding cycles (Table 4.4).

Whereas Joydebpur soil had an initial Eh value of +204 after two weeks flooding of the two week aerobic-flooding cycle the Eh was -135 mV and +20 mV at the four weeks aerobic-flooding cycle (Table 4.5). Addition of organic residues enhanced decrease in Eh of both Faridpur and Joydebpur soils. Pan (1985) also found that adding organic matter to soil caused a dramatic decrease in Eh and 7 to 9 times greater sulfide content than the unamended soil treatment under flooded condition.

Mineralization of sulfur

The relationship between cumulative $\text{SO}_4\text{-S}$ in soils treated with organic residues is shown in figures 4.1 and 4.2. Cumulative SO_4 in all soils treated with narrow C:S ratio of wheat straw (100:1) showed a significantly higher value over control or straw with wide C:S ratio (400:1) under both two or four weeks aerobic-flooding cycles. This follows a similar trend for aerobic soils reported by Barrow (1960) that immobilization of SO_4 occurs in aerobic soil when added organic residue has a C:S ratio above 400.

Except for four weeks aerobic-flooding cycles in Joydebpur soil, water soluble Fe^{2+} values were remarkably low ($<1 \text{ mg Fe}^{2+} \text{ kg}^{-1}$ soils) in straw amended soils (Table 4.6 and 4.7) indicating less reduction of Fe^{3+} to Fe^{2+} during flooding times.

The potentially mineralizable S pool (S_0) and first-order rate constant (K_s) for soils amended with organic residues and incubated under aerobic-flooding

cycles are given in Table 4.8. In calculating the S mineralization constants, the initial extractable SO_4 values were subtracted from the cumulative SO_4 values.

The K_s values for unamended Faridpur and Joydebpur soils ranged from 0.112 to 0.134 $\text{mg S kg}^{-1} \text{wk}^{-1}$ and from 0.149 to 0.160 $\text{mg S kg}^{-1} \text{wk}^{-1}$, respectively. The K^s values from straw treated soils ranged from 0.030 to 0.134 $\text{mg S kg}^{-1} \text{wk}^{-1}$ in Faridpur and from 0.043 to 0.149 $\text{mg S kg}^{-1} \text{wk}^{-1}$ in Joydebpur soil. Among the two C:S ratios, wheat straw with a ratio of 100:1 had the highest rate constants in both two or four weeks aerobic-flooding cycles.

The S_0 values were two to three times greater in straw amended soils compared to control treatment in four weeks aerobic-flooding cycles. Among the two C:S ratios of the straw treatments, the S_0 was 1.5 to 2 times higher with soil amended with narrow C:S ratio (100:1) straw than a wider C:S ratio straw (400:1). The low S_0 of soils amended with a wide C:S ratio (400:1) is likely due to immobilization of SO_4 as proposed by Barrow (1960).

Among the two or four weeks aerobic-flooding cycles, two weeks aerobic-flooding cycles had higher K_s values, indicating higher rates of S mineralization. This is consistent with the work of Williams (1967) who found that drying-wetting cycles in soil increased S mineralization. Conversely, straw materials under four week aerobic-flooding cycles had the highest S_0 values in the soils.

Carbon mineralization

The cumulative amounts of C mineralized were linear with time of incubation (Figs. 4.3 and 4.4). Table 4.9 shows the intercepts and slopes (rates) of the regression equations for the linear relationship between cumulative C mineralized in soils and time of aerobic-flooding incubation. All the relationships were significant at the <0.001 probability level.

The slopes of the regression equation (rate of C mineralization) in unamended soils ranged from 0.014 to 0.019 mg C kg⁻¹ wk⁻¹. For the straw amended soils the slopes ranged from 0.027 to 0.042 mg C kg⁻¹ wk⁻¹. Compared to control the C mineralization rates were two to three times more in straw treatments. Two or four weeks aerobic-flooding cycles had similar in rates of C mineralization.

For decomposition of alfalfa under aerobic conditions, Gale and Gilmour (1988) reported C mineralization (using CO₂ evolution) rate constants values of 0.861, 0.413, and 0.067 mg C kg⁻¹ wk⁻¹ for rapid, intermediate, and slow phases of decomposition, respectively.

Correlation between Soil Properties and S Mineralization Parametres under Aerobic-Flooding Cycles

The matrix correlation (r) among properties of soils measured over 12 week aerobic-flooding incubation are shown in Tables 4.10 and 4.11. Only cumulative SO₄ content of Faridpur soil in two week aerobic-flooding cycles incubation showed a significant correlation with soluble organic C (SOC) content (Table 4.10). The HCO₃ content of both the soils showed a significant correlation with SO₄,

cumulative S and SOC content of the soils in a four week aerobic-flooding cycle, and with SO_4 content of the soils in a two week aerobic flooding cycles.

CONCLUSIONS

The potentially mineralizable S pool (S_0) and first-order rate constants (K_s) in soils amended with wheat (*Triticum aestivum* L.) straw with narrow C:S ratio (100:1) or wide C:S ratio (400:1) incubated under aerobic-flooding cycles were estimated using exponential equation of Standford and Smith (1972). The C:S ratio of wheat straw was a major factor in determining rates of S mineralization in soils. Evidence for this was that the straw with a narrow ratio of 100:1 had much higher cumulative amounts of SO_4 -S, and higher K_s and S_0 values. More frequent aerobic-flooding cycles favored S mineralization.

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Table 4.1. Chemical properties of the Stephen wheat straw used in the incubation study.

Properties	Wheat straw [†]	
	0	80 mg S kg ⁻¹
Total Organic C (g kg ⁻¹)	363	400
Total S (g kg ⁻¹)	0.87	3.99
Total N (g kg ⁻¹)	58.7	46.7
Total P (g kg ⁻¹)	4.9	3.6
C:S ratio	417	100
C:N ratio	6.18	8.57
C:P ratio	74	111
N:S ratio	67.47	11.70
HI reducible S (mg kg ⁻¹)	60	1269
C-bonded S (mg kg ⁻¹)	49.41	53.41
Reduced S (mg kg ⁻¹)	4.67	17.01
Residual S (mg kg ⁻¹)	756	2650

[†]Stephen wheat grown in the greenhouse with S level of 0 or 80 mg S kg⁻¹ soil.

Table 4.2. Effect of organic residue addition on the pH of a Faridpur soil measured during a 12 week incubation under aerobic-flooding cycles.

Residue Treatments	Weeks					
	2	4	6	8	10	12
	Aerobic	Flooded	Aerobic	Flooded	Aerobic	Flooded
Control	--	7.90	--	7.82	--	7.83
C:S ₄₀₀	--	7.85	--	7.79	--	7.67
C:S ₁₀₀	--	7.80	--	7.70	--	7.71
	Aerobic	Aerobic	Flooded	Flooded	Aerobic	Aerobic
Control	--	--	7.83	7.53	--	--
C:S ₄₀₀	--	--	7.67	7.49	--	--
C:S ₁₀₀	--	--	7.64	7.46	--	--

Table 4.3. Effect of organic residue addition on the pH of a Joydebpur soil measured during a 12 week incubation under aerobic-flooding cycles.

Residue Treatments	Weeks					
	2	4	6	8	10	12
	Aerobic	Flooded	Aerobic	Flooded	Aerobic	Flooded
Control	--	7.30	--	7.20	--	7.21
C:S ₄₀₀	--	7.14	--	7.24	--	7.30
C:S ₁₀₀	--	7.38	--	7.36	--	7.35
	Aerobic	Aerobic	Flooded	Flooded	Aerobic	Aerobic
Control	--	--	7.34	7.45	--	--
C:S ₄₀₀	--	--	7.00	7.30	--	--
C:S ₁₀₀	--	--	7.29	7.50	--	--

Table 4.4. Effect of organic residue addition on the redox potential (Eh, mV) of a Faridpur soil measured during a 12 week incubation under aerobic-flooding cycles.

Residue Treatments	Weeks					
	2	4	6	8	10	12
	Aerobic	Flooded	Aerobic	Flooded	Aerobic	Flooded
Control	--	+104	--	+127	--	+126
C:S ₄₀₀	--	+118	--	-126	--	-107
C:S ₁₀₀	--	+93	--	-147	--	-157
	Aerobic	Aerobic	Flooded	Flooded	Aerobic	Aerobic
Control	--	--	+114	+88	--	--
C:S ₄₀₀	--	--	+107	-132	--	--
C:S ₁₀₀	--	--	+58	-145	--	--

Table 4.5. Effect of organic residue addition on the redox potential (Eh, mV) of a Joydebpur soil measured during a 12 week incubation under aerobic-flooding cycles.

Residue Treatments	Weeks					
	2	4	6	8	10	12
	Aerobic	Flooded	Aerobic	Flooded	Aerobic	Flooded
Control	--	-90	--	+22	--	-73
C:S ₄₀₀	--	-26	--	-192	--	-178
C:S ₁₀₀	--	-292	--	-207	--	-165
	Aerobic	Aerobic	Flooded	Flooded	Aerobic	Aerobic
Control	--	--	-112	-180	--	--
C:S ₄₀₀	--	--	+60	-132	--	--
C:S ₁₀₀	--	--	+114	-202	--	--

Table 4.6. Cumulative amount of water soluble iron (Fe^{2+}) in a Faridpur soil ($\text{mg Fe}^{2+} \text{ kg}^{-1}$ soil) amended with organic residues under aerobic-flooding cycles.

Residue Treatments	Weeks					
	2	4	6	8	10	12
2 weeks aerobic-flooding cycles						
Control	0.07	0.16	2.36	2.96	4.60	4.82
C:S ₄₀₀	0.04	0.14	0.46	0.50	0.82	0.92
C:S ₁₀₀	0.00	0.06	0.12	0.20	0.40	0.52
4 weeks aerobic-flooding cycles						
Control	0.08	0.49	0.73	0.86	2.84	5.64
C:S ₄₀₀	0.04	0.13	0.22	0.26	0.66	0.95
C:S ₁₀₀	0.02	0.08	0.18	0.22	0.36	0.48

Table 4.7. Cumulative amount of water soluble iron (Fe^{2+}) in a Joydepur soil ($\text{mg Fe}^{2+} \text{ kg}^{-1}$ soil) amended with organic residues under aerobic-flooding cycles.

Residue Treatments	Weeks					
	2	4	6	8	10	12
2 weeks aerobic-flooding cycles						
Control	0.00	0.08	0.47	0.57	1.49	2.08
C:S ₄₀₀	0.04	0.08	0.23	0.29	0.47	0.59
C:S ₁₀₀	0.08	0.20	0.33	0.41	0.61	0.67
4 weeks aerobic-flooding cycles						
Control	0.04	0.38	0.68	0.87	5.67	10.87
C:S ₄₀₀	0.05	0.07	0.21	0.35	2.19	4.51
C:S ₁₀₀	0.06	0.12	0.20	0.31	1.73	5.61

Table 4.8. Sulfur mineralization constants[†] for soils amended with organic residues and incubated under aerobic-flooding cycles.

Residue treatments	Faridpur soil			Joydebpur soil		
	S ₀	K	R ² [‡]	S ₀	K	R ² [‡]
2 weeks aerobic-flooding cycles						
Control	39.76	0.134	0.95	36.21	0.160	0.97
C:S ₄₀₀	21.00	0.124	0.97	31.90	0.090	0.93
C:S ₁₀₀	60.51	0.134	0.98	75.29	0.136	0.99
4 weeks aerobic-flooding cycles						
Control	35.19	0.112	0.95	35.72	0.149	0.96
C:S ₄₀₀	48.62	0.030	0.95	67.59	0.043	0.95
C:S ₁₀₀	100.24	0.113	0.96	102.30	0.124	0.96

[†]S₀ = Potential mineralizable S (mg S kg⁻¹ soil) and K = first-order rate constant (mg S kg⁻¹ wk⁻¹).

[‡]Significant at P < 0.05.

Table 4.9. Parameters and R-squared linear relationships between cumulative C mineralized (mg C kg^{-1} soil), y, and incubation time (wk^{-1}), x, under aerobic-flooding cycles.

Residue treatments	Faridpur soil			Joydebpur soil		
	Intercept	Slope	R^2 [†]	Intercept	Slope	R^2 [†]
2 weeks aerobic-flooding cycles						
Control	-0.003	0.014	0.97	-0.007	0.019	0.97
C:S ₄₀₀	-0.001	0.030	0.97	0.008	0.042	0.95
C:S ₁₀₀	-0.004	0.031	0.97	0.008	0.031	0.96
4 weeks aerobic-flooding cycles						
Control	-0.013	0.015	0.89	-0.006	0.018	0.97
C:S ₄₀₀	-0.011	0.032	0.91	-0.033	0.035	0.93
C:S ₁₀₀	-0.018	0.027	0.95	-0.007	0.028	0.95

[†]Significant at $P < 0.001$.

Table 4.10. Matrix of correlation coefficients (r)[†] between various properties measured over 12 week incubation of a Faridpur soil under aerobic-flooding cycles.

Properties	SO ₄ -S	cum S [‡]	SOC [§]	HCO ₃
2 weeks aerobic-flooding cycles				
SO ₄ -S	--	-0.11	0.23	0.38*
cum S		--	0.31*	0.25
SOC			--	0.83***
4 weeks aerobic-flooding cycles				
SO ₄ -S	--	0.25	0.11	0.30*
cum S		--	0.27	0.36*
SOC			--	0.76***
HCO ₃				--

***, ***, *Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 42 in each aerobic-flooding cycles.

[‡]cum S = cumulative SO₄-S.

[§]SOC = soluble organic carbon.

Table 4.11. Matrix of correlation coefficients (r)[†] between various properties measured over 12 week incubation of a Joydebpur soil under aerobic-flooding cycles.

Properties	SO ₄ -S	cum S [‡]	SOC [§]	HCO ₃
2 weeks aerobic-flooding cycles				
SO ₄ -S	--	-0.05	0.16	0.41 ^{**}
cum S		--	0.16	0.25
SOC			--	0.81 ^{***}
4 weeks aerobic-flooding cycles				
SO ₄ -S	--	0.09	0.20	0.29 [*]
cum S		--	0.27	0.31 [*]
SOC			--	0.81 ^{***}
HCO ₃				--

^{*, **, ***}Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 42 in each aerobic-flooding cycles.

[‡]cum S = cumulative SO₄-S.

[§]SOC = soluble organic carbon.

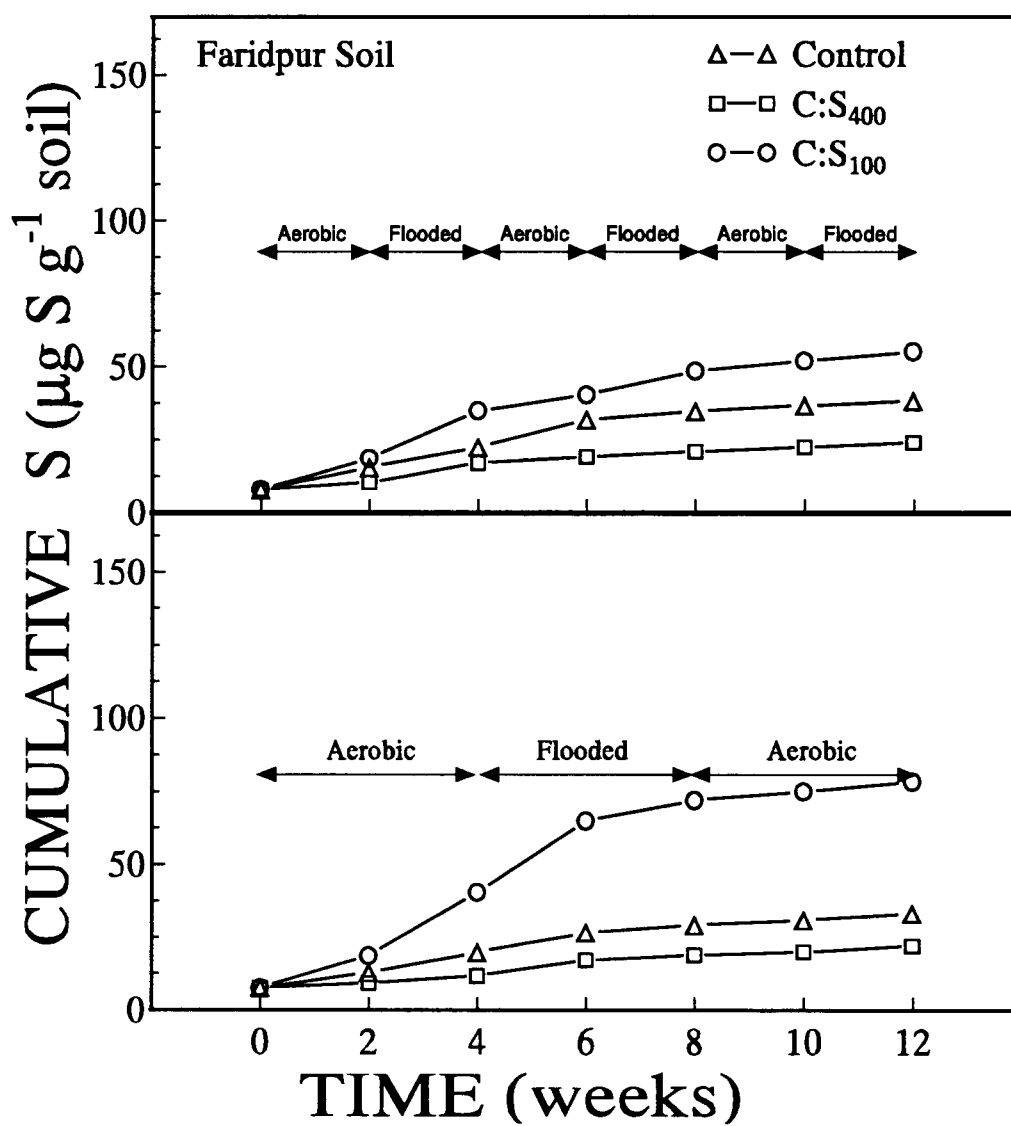


Figure 4.1. Cumulative amount of $\text{SO}_4\text{-S}$ in a Faridpur soil amended with organic residues under aerobic-flooding cycles.

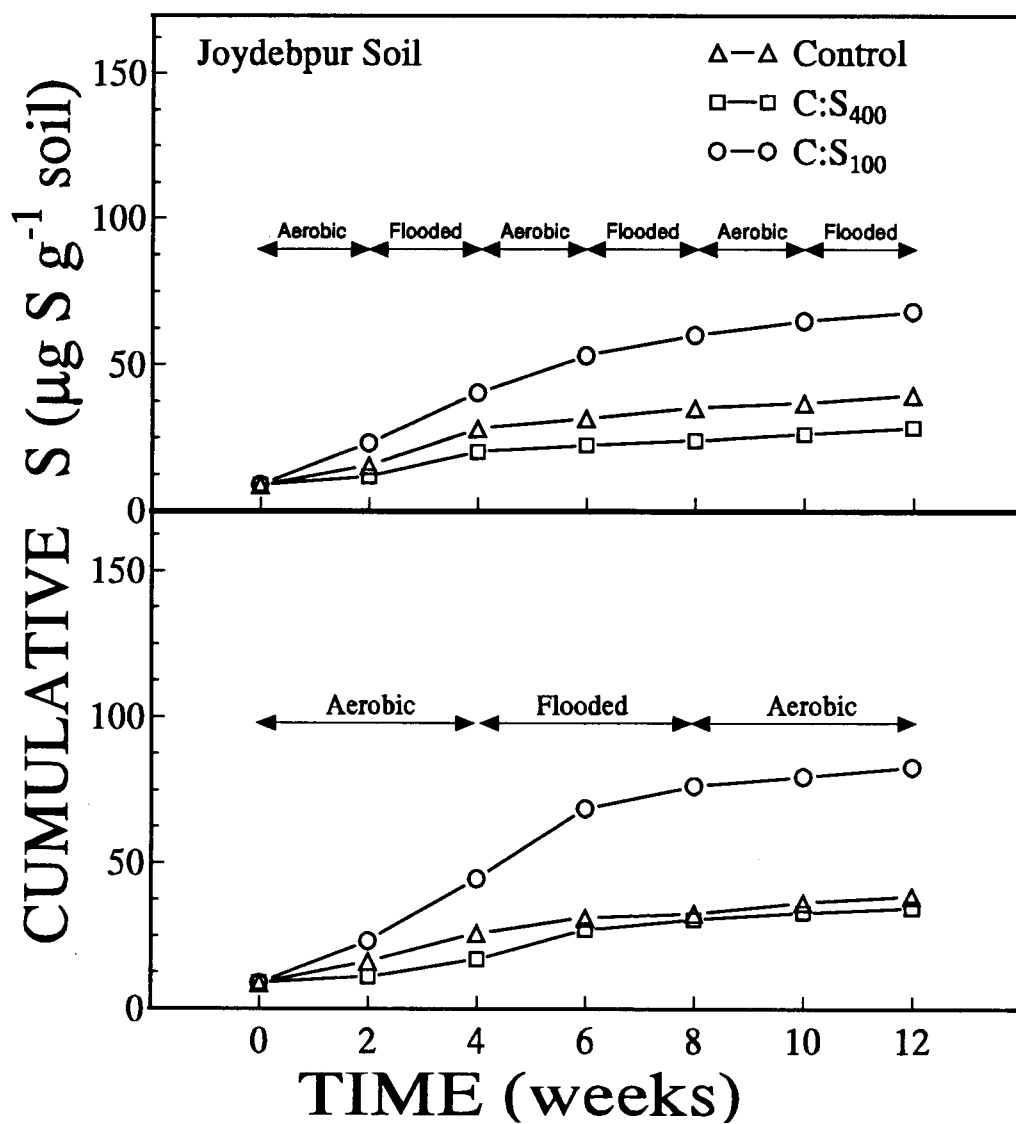


Figure 4.2. Cumulative amount of $\text{SO}_4\text{-S}$ in a Joydebpur soil amended with organic residues under aerobic-flooding cycles.

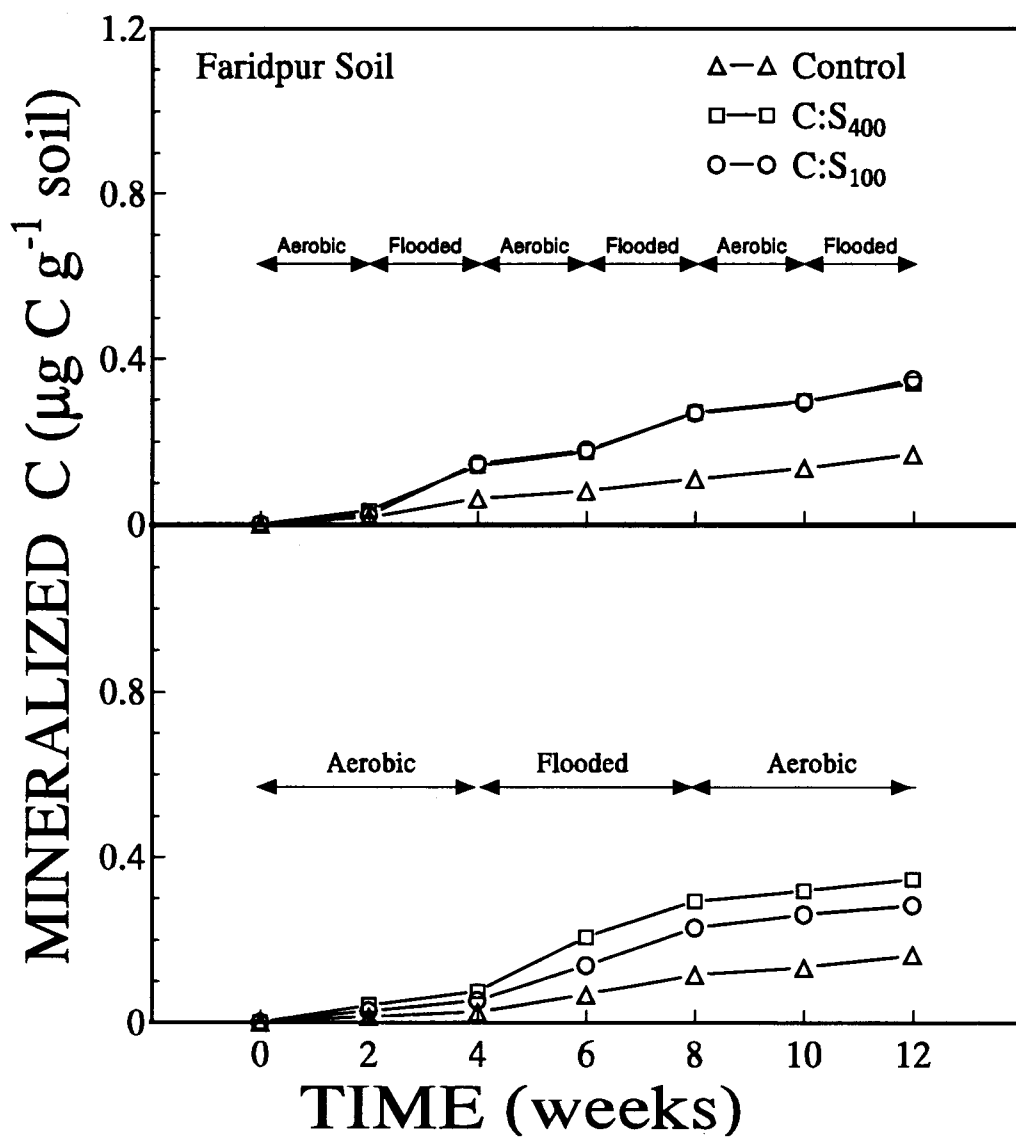


Figure 4.3. Cumulative amount of mineralized C in a Faridpur soil amended with organic residues under aerobic-flooding cycles.

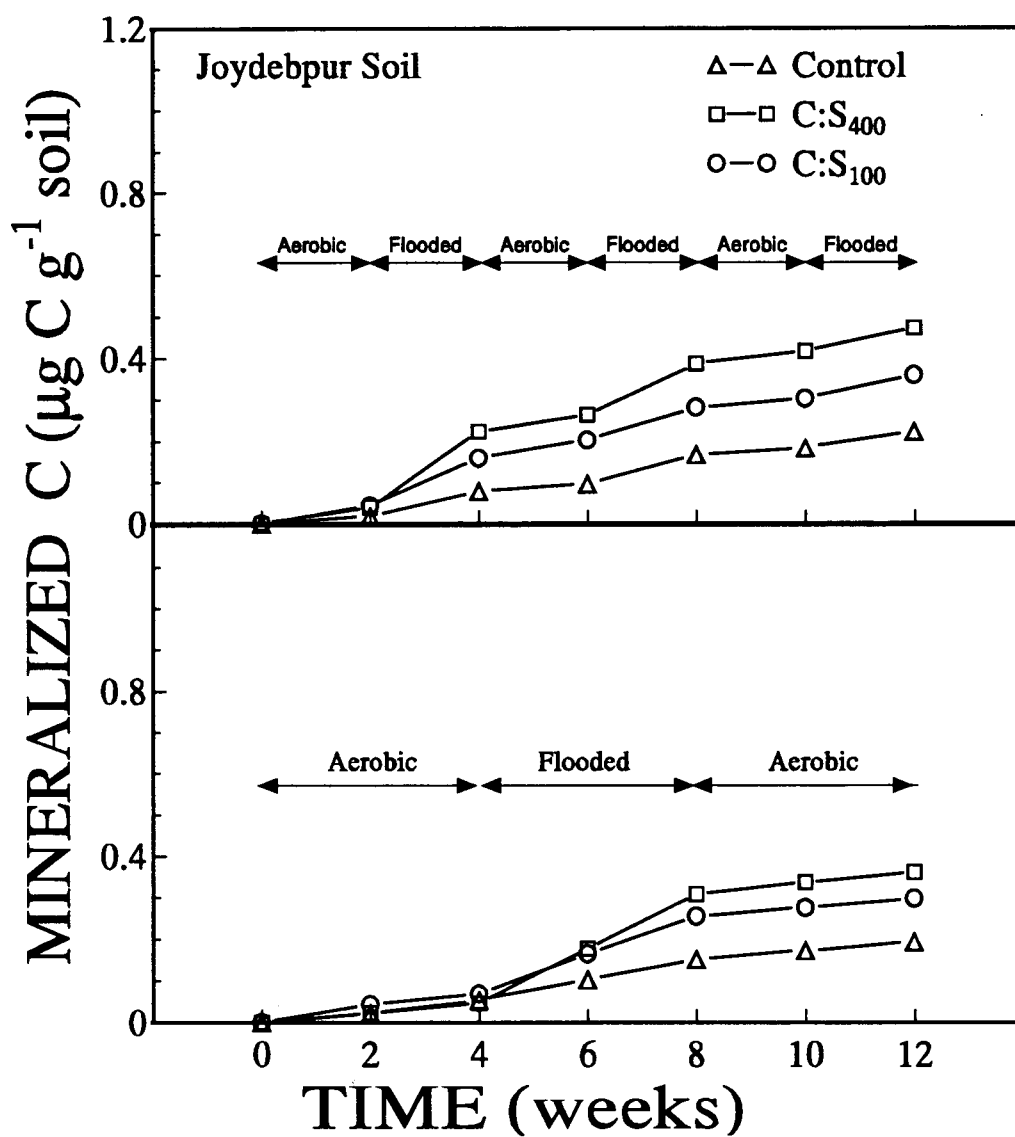


Figure 4.4. Cumulative amount of mineralized C in a Joydebpur soil amended with organic residues under aerobic-flooding cycles.

CHAPTER V

EFFECT OF RESIDUE C:S RATIO ON THE MINERALIZATION OF NITROGEN IN SOILS UNDER AEROBIC-FLOODING CYCLES

ABSTRACT

This study was undertaken to assess the effect of organic residue C:S ratio on the mineralization of N in rice soils under aerobic-flooded conditions. A lab incubation study was conducted that had a 3 x 2 x 2 factorial design (two replications) with two rice soils (Faridpur and Joydebpur), three wheat (*Triticum aestivum* L.) straw amendments (control, 400:1 or 100:1) C:S ratio straw; and two moisture levels (two or four week aerobic-flooding cycles).

Cumulative N ($\text{NO}_3 + \text{NH}_4\text{-N}$) mineralized in all the soils amended with wheat straw showed a significantly higher value over unamended control. Soil amended with wheat straw that had a narrow C:S ratio (100:1) produced a higher cumulative N than a wide C:S ratio straw (400:1). After 12 weeks incubation, a four week aerobic-flooding cycle had 1.3 to 2.9 times more mineralized N than a two week aerobic-flooding cycle. Relatively low cumulative N in two week aerobic-flooding cycles was probably due to higher denitrification loss, since frequent wetting and drying creates favorable condition for denitrification. Potentially mineralizable N pool (N_0) and first-order rate constants (K_N) in soils amended with wheat straw and incubated under aerobic-flooding cycles were estimated by using the exponential equation. The K_N values for unamended soils ranged from 0.326 to 0.537 $\text{mg N kg}^{-1} \text{wk}^{-1}$. Conversely, K_N values in wide C:S ratio and narrow C:S ratio ranged from 0.187 to 0.286 and 0.275 to 0.351 $\text{mg N kg}^{-1} \text{wk}^{-1}$, respectively. Lower K_N values in straw treated soils were due to immobilization of N compounds. The N_0 values in straw treated soils were 2 to 5.7 times more than

the unamended control treatment. Among the two C:S ratios of the straw, N_0 were 1 to 2.7 times more in narrow C:S ratio straw (100:1) than the wide C:S ratio straw (400:1). Cumulative N (NO_3+NH_4-N) content of the soils was significantly correlated with SOC content of the soils.

INTRODUCTION

Nitrogen (N) in soils undergoes many transformations. A large proportion of soil N is organically bound N with only a small amount as inorganic fractions. Organic N forms the potential reserve of N for the nutrition of plants but is available to plants only after it has been converted to an inorganic form (Tusneem and Patrick, 1971). Nitrogen transformations in submerged soils and sediments are markedly different from well drained aerobic soils (Patrick, 1982).

Standford and Smith (1972) proposed an open incubation leaching technique to study the N mineralization potentials of aerobic soils and reported that the cumulative net N mineralized was linearly related to the square root of time ($t^{1/2}$). Using the same incubation technique Tabatabai and Al-Khafaji (1980) found a linear relationship between the cumulative amount of N and S mineralized with time of incubation in aerobic soil.

In a sulfur (S) mineralization study under laboratory conditions, differences in net S mineralization rates have been observed between open and closed soil-incubation systems (Maynard et al., 1983). The open system gives significantly higher results and may simulate, by periodic leaching, the removal of N and S by plants or loss of these elements through leaching processes (Tabatabai and Al-Khafaji, 1980).

Nitrogen mineralization potentials and rate constants in soils amended with rice (*Oryza sativa* L.) straw and pea vine (*Pisum sativum* L.) under flooded conditions were estimated in Chapter II using exponential equations and leaching techniques of Standford and Smith (1972). The rate constants (K_N) of rice straw treated

soils were 1.5 to 3.5 times more than the unamended control. Soils amended with rice straw had 7 to 15 times, and pea vine had 3 to 9 times more cumulative N potential (N_0) than the control.

Rice soils are often subjected to alternate wetting and drying due to uncertainties of natural rainfall or due to intermittent drainage of flooded rice fields during the growing season (Patrick and Mahapatra, 1968). Therefore, understanding the process of N mineralization under flooded as well as under alternate wetting and drying is important with respect to N availability to rice.

Little is known about N mineralization rates and potentials of rice soils under alternate wetting-drying cycles. Therefore, the objective of this study was to determine the effect of organic residue C:S ratios on the potentially mineralizable N pool and first order rate constants in rice soils under aerobic-flooding cycles.

MATERIALS AND METHODS

The soils used were surface soils (0-15 cm) selected to represent the large rice growing areas of Bangladesh. Soil sample preparation and chemical and physical analyses of the soils were reported in Chapter I. Chemical analyses of the wheat straw materials used in the incubation study were reported in Chapter IV.

Incubation Procedure

The details of the incubation procedure were reported in Chapter IV. In brief, the study was a 3 x 2 x 2 factorial experiment with two rice soils (Faridpur and Joydebpur); three levels of wheat (*Triticum aestivum* L.) straw (control or straw

with C:S ratio 400:1 or 100:1); and two moisture levels (two or four week aerobic-flooding cycles).

Thirty g of air dried soil and an equal weight of glass beads (0.45 to 0.52 mm diameter) were mixed thoroughly with wheat straw (25 mg g⁻¹ soil) and transferred into leaching tubes. Soils in the leaching tubes were incubated at 35°C in an incubator as aerobic (75% of field capacity) or flooded by adding 50 mL deionized (DI) water in each leaching tube.

Soil-glass bead mixtures were leached with 60 mL DI water at two weeks intervals up to 12 weeks. All incubations were carried out in duplicate. Leachate was analyzed for NO₃-N using Dionex ion chromatography and NH₄-N by steam distillation (Bremner and Keeney, 1965). The exponential equation proposed by Stanford and Smith (1972) was used to measure potentially mineralizable N pool (N₀) and first-order rate constant (K_N) by the following equation:

$$N_m = N_0[1 - \exp(-K_N t)]$$

where N_m = N mineralized under aerobic-flooding cycles incubation at specific time (t).

RESULTS AND DISCUSSION

Accumulation of Inorganic N

The relationship between cumulative inorganic N (NO₃+NH₄-N) in soils treated with organic residues and time of aerobic-flooding incubation is shown in Figures 5.1 and 5.2. Cumulative inorganic N in all the soils amended with wheat

straw (C:S ratio of 400:1 or 100:1) showed significantly higher values over the unamended control. The narrow C:S ratio (100:1) produced greater cumulative inorganic N than the wide C:S ratio (400:1). After 12 weeks incubation period, four weeks aerobic-flooding cycle had 1.3 to 2.9 times more cumulative N over two weeks aerobic-flooding cycles (Figs. 5.1 and 5.2).

Lower cumulative inorganic N in the two weeks aerobic-flooding cycle was probably due to higher denitrification losses. Alternate wetting and drying conditions create ideal conditions for denitrification. Nitrate formed during the dry period is rapidly lost through denitrification when the soil is reflooded (Tusneem and Patrick, 1971). Patrick and Wyatt (1964) observed large losses of N (up to 20% of total N), as a result of several drying and submergence cycles.

The potentially mineralizable N pool (N_0) and first-order rate constants (K_N) for soils amended with organic residues and incubated under aerobic-flooding cycles are given in Table 5.1. In calculating the cumulative inorganic N (NO_3+NH_4-N) constants, the initial extractable inorganic N values were subtracted from the cumulative inorganic N (NO_3+NH_4-N) values.

The K_N values for unamended treatment in both the soils were higher than the straw treatments (Table 5.1). The K_N values in wide C:S ratio (400:1) and narrow C:S ratio (100:1) treated soils ranged from 0.187 to 0.286 and 0.275 to 0.351 mg N kg⁻¹ wk⁻¹, respectively. Conversely, the K_N values in unamended soils ranged from 0.326 to 0.537 mg N kg⁻¹ wk⁻¹. Harmsen and Kolenbrander (1965) reported that the C:N ratio of decomposing material must be below 20 to 25 for an appreciable net mineralization. Although the straw residue treatments had lower

C:N ratio (chapter IV, Table 4.1), the lower K_N values in straw treated soils suggesting that some other factor such as biology of the soil may be playing a role in N mineralization.

The N_0 in straw treated soils were 2 to 5.7 times more than the unamended control treatment (Table 5.1). Among the two C:S ratio of the straw treatments, the N_0 were 1 to 2.7 times more in narrow C:S ratio than the wide C:S ratio (400:1) treated soil. Low values of N_0 in wide C:S ratio (400:1) treated soils were probably due to greater N immobilization with wide N:S ratio of 67:1 with C:S₄₀₀ tissue vs 12:1 in C:S₁₀₀.

Correlation between Soil Properties and N Mineralization Parameters Under Aerobic-Flooding cycles

The matrix correlation coefficients (r) among properties of the soils measured over 12 weeks aerobic-flooding incubation are shown in Tables 5.2 and 5.3.

Under both two or four week aerobic flooding cycles, among the various parameters NH_4 -N was significantly correlated with cumulative N content, SOC with HCO_3 content of the soils, and cumulative N content of the soils were significantly correlated with SOC content of the soils.

CONCLUSIONS

The potentially mineralizable N pool (N_0) and first-order rate constants (K_N) in soils amended with wheat (*Triticum aestivum* L.) straw with narrow C:S ratio

(100:1) or wide C:S ratio (400:1) incubated under aerobic-flooding cycles were estimated using exponential equations of Standford and Smith (1972).

The C:S ratio of the wheat straw was a major factor in determining N_0 in soils. It is evident from the result that the straw with a narrow ratio of 100:1 had the higher cumulative amounts of N and higher N_0 values. Since the straw residue treatments had lower C:N ratio, the lower K_N values in straw treated soils suggest that some other factor such as biology of the soil plays a role in N mineralization process. Lower cumulative N values in soils in two weeks aerobic flooding cycles were considered to be associated with higher denitrification loss due to frequent wetting and drying cycles.

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Table 5.1. Nitrogen mineralization constants[†] for soils amended with organic residues and incubated under aerobic-flooding cycles.

Residue treatments	Faridpur soil			Joydebpur soil		
	N ₀	K _N	R ² [‡]	N ₀	K _N	R ² [‡]
2 weeks aerobic-flooding cycles						
Control	79.32	0.537	0.98	75.04	0.475	0.97
C:S ₄₀₀	166.63	0.219	0.98	227.82	0.286	0.99
C:S ₁₀₀	455.86	0.351	0.99	225.99	0.283	0.97
4 weeks aerobic-flooding cycles						
Control	111.99	0.326	0.93	129.50	0.443	0.90
C:S ₄₀₀	431.33	0.187	0.93	335.45	0.239	0.97
C:S ₁₀₀	628.43	0.275	0.98	391.88	0.287	0.98

[†]N₀ = Potential mineralizable N (mg N kg⁻¹ soil) and K_N = first-order rate constant (mg N kg⁻¹ wk⁻¹).

[‡]Significant at P < 0.05.

Table 5.2. Matrix of correlation coefficients (r)[†] between various properties measured over 12 week incubation of a Faridpur soil under aerobic-flooding cycles.

Properties	NH ₄ -N	NO ₃ -N	Cum N [‡]	SOC [§]	HCO ₃
2 weeks aerobic-flooding cycles					
NH ₄ -N	--	0.13	-0.32 [*]	-0.16	-0.05
NO ₃ -N		--	0.16	0.04	0.05
Cum N			--	0.43 ^{**}	0.27
SOC				--	0.83 ^{***}
HCO ₃					--
4 weeks aerobic-flooding cycles					
NH ₄ -N	--	-0.03	-0.39 [*]	-0.25	-0.17
NO ₃ -N		--	0.17	-0.08	-0.23
Cum N			--	0.45 ^{**}	0.36 [*]
SOC				--	0.76 ^{***}
HCO ₃					--

^{*, **, ***}Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 42 in each aerobic-flooding cycles.

[‡]Cum N = cumulative N.

[§]SOC = soluble organic carbon.

Table 5.3. Matrix of correlation coefficients (r)[†] between various properties measured over 12 week incubation of a Joydebpur soil under aerobic-flooding cycles.

Properties	NH ₄ -N	NO ₃ -N	Cum N [‡]	SOC [§]	HCO ₃
2 weeks aerobic-flooding cycles					
NH ₄ -N	--	-0.21	-0.62 ^{***}	-0.19	-0.07
NO ₃ -N		--	0.06	0.08	-0.15
Cum N			--	0.43 ^{**}	0.25
SOC				--	0.81 ^{***}
HCO ₃					--
4 weeks aerobic-flooding cycles					
NH ₄ -N	--	-0.29	-0.59 ^{**}	-0.33 [*]	-0.26
NO ₃ -N		--	0.0714	-0.03	0.1805
Cum N			--	0.50 ^{**}	0.31 [*]
SOC				--	0.81 ^{***}
HCO ₃					--

^{*,**,***}Significant at the 0.05, 0.01, and 0.001 probability levels, respectively.

[†]n = 42 in each aerobic-flooding cycles.

[‡]Cum N = cumulative N.

[§]SOC = soluble organic carbon.

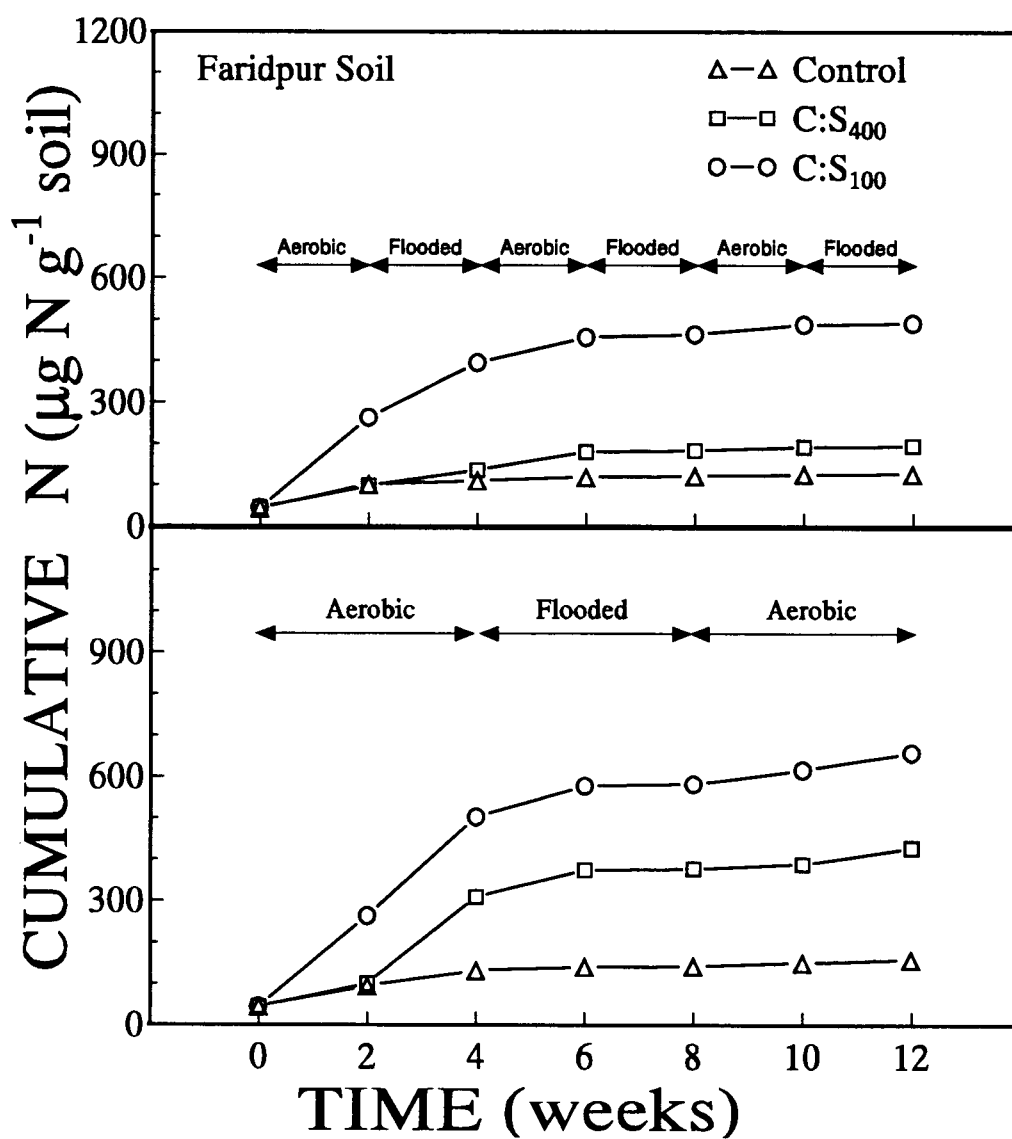


Figure 5.1. Cumulative amount of inorganic N ($\text{NO}_3 + \text{NH}_4\text{-N}$) in a Faridpur soil amended with organic residues under aerobic-flooding cycles.

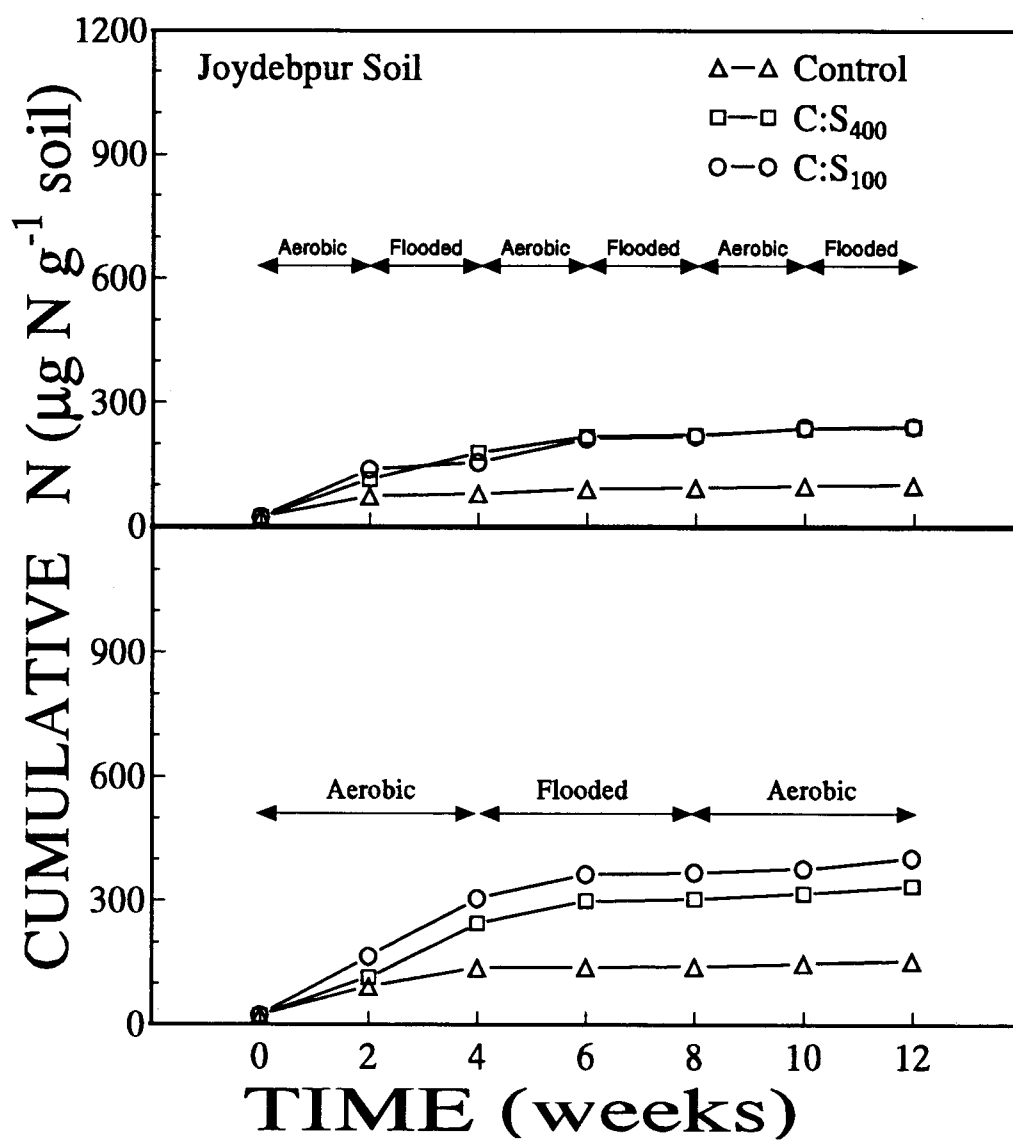


Figure 5.2. Cumulative amount of inorganic N ($\text{NO}_3+\text{NH}_4\text{-N}$) in a Joydebpur soil amended with organic residues under aerobic-flooding cycles.

CHAPTER VI

EFFECT OF RESIDUE C:S RATIO ON THE RELEASE OF PHOSPHORUS IN SOILS UNDER AEROBIC-FLOODING CYCLES

ABSTRACT

This study was undertaken to assess the PO_4 released in rice soils amended with organic residue under aerobic-flooded cycling. A lab incubation study was conducted that had a $3 \times 2 \times 2$ factorial design (two replications) with two rice soils (Faridpur and Joydebpur); three wheat (*Triticum aestivum* L.) straw amendments (control or straw with C:S ratios of 400:1 or 100:1); and two moisture levels (two or four week aerobic-flooding cycles). Air-dried soils and glass beads (1:1) were mixed with wheat straw (25 mg g^{-1} soil) and transferred into leaching tubes. Soils were either flooded by adding deionized water (DI) or under aerobic conditions (75% of field capacity) and were incubated at 35°C for 12 weeks. Every two weeks soils in the leaching tube were leached with DI water and analyzed for phosphate and other chemical properties. The cumulative amount of PO_4 released was linear with time of incubation and all the relationships were significant at the <0.001 probability level. The slope of the regression equation (rate of P mineralization) in unamended soils ranged from 0.74 to $1.07 \text{ mg P kg}^{-1} \text{ wk}^{-1}$. The slopes of the straw amended soils ranged from 0.86 to $1.82 \text{ mg P kg}^{-1} \text{ wk}^{-1}$. Compared to the control, the P mineralization rates were one to two times more in soils treated with wheat straw.

Comparing rate constants showed that within a wheat straw treatment or control K values were quite similar between two and four week aerobic-flooding cycles.

INTRODUCTION

The soil water environment varies widely among rice growing areas.

Although rice is often grown under continuous flooding, alternate flooding-drying conditions also occur as a result of management or due to climatic conditions under rainfed rice production (Patrick and Mahapatra, 1968). Consequently transformations of phosphorus (P) are quite different under aerobic or aerobic-flooding conditions in comparison to continuous flooding.

The availability to rice of native soil P and added P increases after soil submergence (Ponnamperuma 1965; Patrick and Mahapatra, 1968). This increase in P availability in acid soils is associated with a decrease in Eh or an increase in iron (Fe^{+2}). Conversely, in alkaline soils the increase in solubility of P is related to a decrease in pH of these soils on flooding (Stumm and Morgan, 1970). However, the P released by these reactions and from the decomposition of organic matter may be resorbed by clay and hydrous oxides of Al in the anaerobic zone (Bromfield, 1960) or they may diffuse to oxidized zones and be reprecipitated as Fe or Al compounds.

Drying a soil prior to flooding generally decreases the solubilities of both native and added phosphates (Paul and Delong, 1949). Drying leads to the conversion of soluble phosphates to less readily extractable forms and to a decrease in the organic P fraction. The biological reduction of iron during the flooding phase followed by reoxidation during the drying phase results in the enhanced reactivity

of the sesquioxide fraction of the soil, leads to an increase in the phosphate fixing capacity, and hence a decrease in the solubility of P (Paul and Delong, 1949).

Little is known about the release of P in rice soils under alternate wetting and drying conditions. Therefore, this study was undertaken to assess the effect of added organic residues varying in C:S ratios on the P release in some wetland rice soils under aerobic-flooding cycles.

MATERIALS AND METHODS

The soils used were surface soils (0-15 cm) selected to represent the large rice growing areas of Bangladesh. Soil sample preparation and chemical and physical analyses of the soils were reported in Chapter I. Chemical analysis of the wheat straw materials used in the incubation study were reported in Chapter IV.

Incubation Procedure

The details of the incubation procedure were reported in Chapter IV. In brief, the study was a 3 x 2 x 2 factorial experiment with two rice soils (Faridpur and Joydebpur); three levels of wheat (*Triticum aestivum* L.) straw (control or straw with C:S ratio 400:1 or 100:1); and two moisture levels (two or four week aerobic-flooding cycles).

Thirty g of air dried soil and an equal weight of glass beads (0.45 to 0.52 mm diameter) were mixed thoroughly with wheat straw (25 mg g⁻¹ soil) and transferred into leaching tubes. Soils in the leaching tubes were incubated at 35°C

in an incubator for 12 weeks under aerobic conditions (75% of field capacity) or flooded (by adding 50 ml deionized water (DI) in each leaching tube) conditions.

Soil:glass bead mixtures were leached with 60 mL DI water at two weeks intervals up to 12 weeks to remove available PO_4 released in soil. All incubations were carried out in duplicate. Leachate obtained was analyzed for PO_4 using a Dionex ion chromatograph.

RESULTS AND DISCUSSION

The relationship between cumulative PO_4 and incubation time as affected by wheat straw is shown in Figures 6.1 and 6.2. Cumulative P in all the soils treated with wheat straw showed a higher accumulation of PO_4 over control treatment.

Table 6.1 shows the intercepts and slopes (rates of release) of the regression equations for the linear relationship between cumulative P released in both the Faridpur and Joydebpur soils and time of aerobic-flooding incubation. All the linear relationships were significant at the <0.001 probability level. The slopes of the regression equation (rate of P release) in unamended soils ranged from 0.74 to 1.07 $\text{mg kg}^{-1} \text{wk}^{-1}$. Conversely, the slopes of the straw amended soils ranged from 0.86 to 1.82 $\text{mg kg}^{-1} \text{wk}^{-1}$. Compared to the control the P release rates were 1 to 2 times higher in soils treated with wheat straw.

Except for the four weeks aerobic-flooding cycles in Joydebpur soil, water soluble iron (Fe^{2+}) values were very low (Chapter IV, Tables. 4.6 and 4.7), indicating less reduction of the soils during flooding period. This suggests that the higher

PO_4 levels were the result of biological mineralization from the organic residues rather than release from inorganic P compounds. In addition, organic acids such as oxalate can increase the solubility of P in soils through the formation of stable complexes with Al (Marteel et al, 1988). Ligand-exchange reactions between oxalate and P at oxide surfaces directly release P in solution (Stumm, 1986).

Depending on the soil type, the linear rate constants within straw treatments or control showed a similar P release pattern between two and four weeks aerobic-flooding cycles (table. 6.1). The matrix of correlation coefficients (Tables. 6.2 and 6.3) showed that the PO_4 content of the soils were significantly correlated with cumulative P, SOC and HCO_3 content of the soils over 12-weeks period in both two or four weeks aerobic-flooding cycles. In both soils, cumulative iron (Fe^{2+}) showed a significant correlation with cumulative P content.

CONCLUSIONS

Cumulative PO_4 released in all the soils treated with wheat straw was considerably higher than the control treatment, both under two or four weeks aerobic-flooding cycles. The higher PO_4 release in straw treatments was assumed to be due to microbial mineralization of organic residues, rather than release from inorganic P compounds. Phosphate release in both the soils showed a linear relationship with time of incubation and two or four week aerobic-flooding cycles. Regardless of soil types and straw amendments, P release in two or four week aerobic-flooding cycles showed a similar P release pattern.

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Table 6.1. Parameters and R-squared linear relationships between cumulative P mineralized in soils (mg P kg⁻¹ soil) (Y) and incubation time (wk⁻¹) (X) under aerobic-flooding cycles.

Residue treatments	Faridpur soil			Joydebpur soil		
	Intercept	Slope	R ² [†]	Intercept	Slope	R ² [†]
2 weeks aerobic-flooding cycles						
Control	-1.37	1.06	0.94	-0.98	0.74	0.94
C:S ₄₀₀	-2.45	1.82	0.95	-1.50	1.39	0.95
C:S ₁₀₀	-1.69	1.32	0.94	-0.54	0.86	0.97
4 weeks aerobic-flooding cycles						
Control	-1.66	1.07	0.93	-1.03	0.82	0.95
C:S ₄₀₀	-2.27	1.52	0.93	-1.83	1.20	0.93
C:S ₁₀₀	-1.91	1.34	0.93	-0.94	0.97	0.95

[†]Significant at P < 0.001.

Table 6.2. Matrix of correlation coefficients (r)[†] between various properties measured over 12 week incubation of a Faridpur soil under aerobic-flooding cycles.

Properties	PO ₄ -P	Cum P [‡]	SOC [§]	HCO ₃	Cum Fe [¶]
2 weeks aerobic-flooding cycles					
PO ₄ -P	--	0.81 ^{***}	0.58 ^{***}	0.44 ^{**}	0.17
Cum P		--	0.24	0.12	0.34 [*]
SOC			--	0.83 ^{***}	-0.14
HCO ₃				--	-0.10
Cum Fe					--
4 weeks aerobic-flooding cycles					
PO ₄ -P	--	0.59 ^{***}	0.75 ^{***}	0.78 ^{***}	0.15
Cum P		--	0.24	0.19	0.42 ^{**}
SOC			--	0.76 ^{***}	-0.10
HCO ₃				--	-0.04
Cum Fe					--

^{*,**,***}Significant at the 0.05, 0.01 and 0.001 probability levels, respectively.

[†]n = 42 in each aerobic-flooding cycle.

[‡]Cum P = cumulative PO₄-P.

[§]SOC = soluble organic carbon.

[¶]Cum Fe = cumulative iron (Fe²⁺).

Table 6.3. Matrix of correlation coefficients (r)[†] between various properties measured over 12 week incubation of a Joydebpur soil under aerobic-flooding cycles.

Properties	PO ₄ -P	Cum P [‡]	SOC [§]	HCO ₃	Cum Fe [¶]
2 weeks aerobic-flooding cycles					
PO ₄ -P	--	0.71 ^{***}	0.65 ^{***}	0.49 ^{***}	0.29
Cum P		--	0.23	0.13	0.54 ^{***}
SOC			--	0.81 ^{***}	-0.06
HCO ₃				--	-0.02
					--
4 weeks aerobic-flooding cycles					
PO ₄ -P	--	0.52 ^{***}	0.86 ^{***}	0.74 ^{***}	0.01
Cum P		--	0.24	0.11	0.62 ^{***}
SOC			--	0.81 ^{***}	-0.21
HCO ₃				--	-0.21
Cum Fe					--

^{***}Significant at the 0.05, 0.01 and 0.001 probability levels, respectively.

[†]n = 42 in each aerobic-flooding cycle.

[‡]Cum P = cumulative PO₄-P.

[§]SOC = soluble organic carbon.

[¶]Cum Fe = cumulative iron (Fe²⁺).

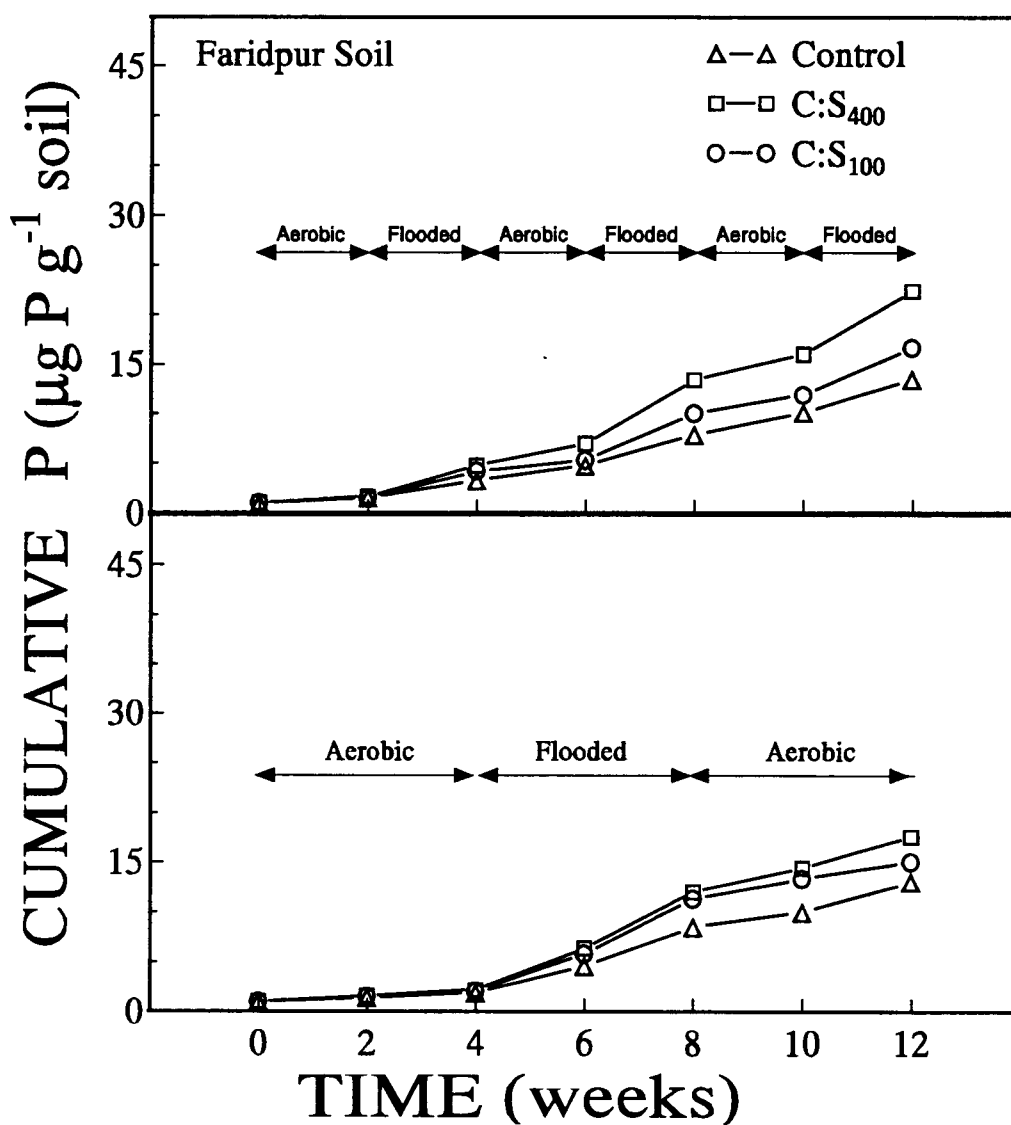


Figure 6.1. Cumulative amount of $\text{PO}_4\text{-P}$ released in a Faridpur soil amended with organic residues under aerobic-flooding cycles.

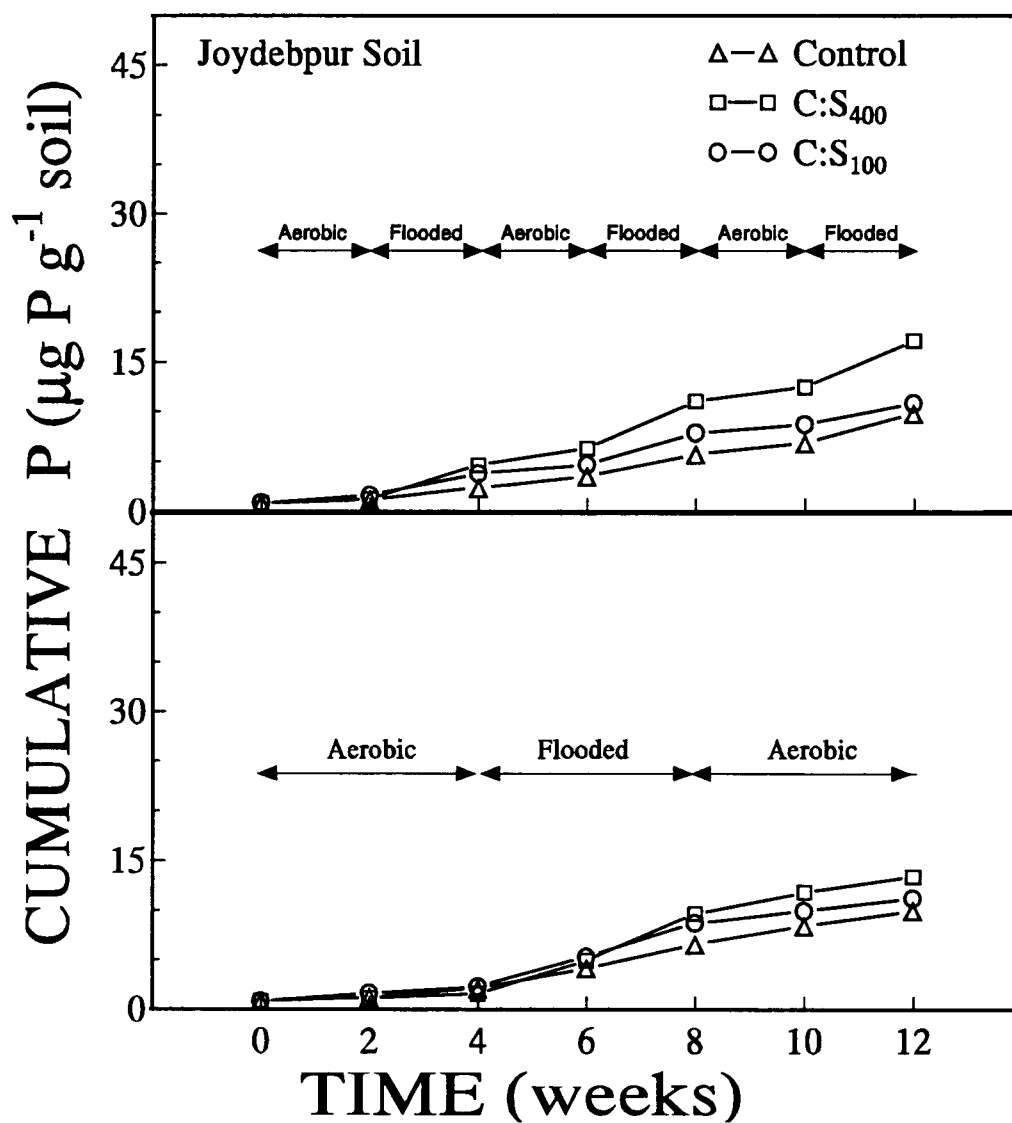


Figure 6.2. Cumulative amount of $\text{PO}_4\text{-P}$ released in a Joydebpur soil amended with organic residues under aerobic-flooding cycles.

CHAPTER VII

EFFECT OF ADDED ORGANIC RESIDUES ON THE
TRANSFORMATIONS OF SULFUR IN SOIL UNDER
CONTINUOUS FLOODING OR AEROBIC-FLOODING CYCLES

ABSTRACT

This study was carried out to determine the effect of C:S ratio of organic residues on the transformation of organic S in wetland rice soil under continuous flooding or aerobic-flooding cycles. A lab incubation study with a 3 x 2 factorial design (three replications) was carried out for 12 weeks. The treatments were: three levels of wheat straw (straw with C:S ratio of 400:1 or 100:1 or control) added to soil (25 mg g⁻¹ soil) and two moisture levels [continuous flooding or aerobic (75% of field capacity)-flooding cycles]. At two week intervals tubes containing 30 g soil were destructively sampled and analyzed for soil chemical and biological properties. Distribution of S fractions (% of total S) in soil showed a considerable increase in the ester S and reduced S fractions and decreases in C-bonded S and SO₄-S fraction under continuous flooding condition. Conversely, the SO₄-S and the residual S fraction (unknown S compounds resistant to hydrolysis by strong acid or base) was significantly increased in wetting-drying cycles with time of incubation. Under flooded conditions plant residue S with a narrow C:S ratio was largely converted to ester S and sulfide. Starting with aerobic conditions caused a rapid accumulation of SO₄ to be released from plant residue. After 12 weeks of aerobic-flooding cycling there was a gradual but relatively large increase in the residual S pool. This demonstrates preliminary information that aerobic-flooding conditions provide significantly more plant available SO₄-S than under continuous flooding (4 to 8 times more).

INTRODUCTION

Sulfur (S) is an essential element for both plants and animals. In soils S is present in both inorganic and organic form. Of the two forms of S in soil, organic S occupies more than 95% of the total S content of the soil (Tabatabai and Bremner, 1972; Tabatabai, 1984). Since S is taken up by plants mostly in the form of SO_4 , the organic forms of S must be mineralized to SO_4 by soil organisms to be available for plant uptake (Brady, 1974; Williams, 1975).

Sulfur mineralization in soils is biological in nature, and the amount of S mineralized in soils depends on soil physical and chemical properties (Pirela and Tabatabai, 1988); types of organic residues (Tabatabai and Chae, 1991); and moisture, aeration, temperature and pH (Brady, 1974). Mineralization and immobilization of S are opposing processes in soils that occur simultaneously (Tusneem and Patrick, 1971). Immobilization of inorganic S occurs when low S, C rich organic materials are added to soils not adequately supplied with inorganic S. Barrow (1960) reported that organic residues added to soil with a C:S ratio of less than 200 caused mineralization but residues with a C:S ratio above 400 caused immobilization of S.

Since most rice production utilizes flooded soils, submergence of a soil creates unique chemical and biological conditions which markedly affect S transformations (Freney and Boonjawat, 1983). Rice soils are often subjected to alternate wetting and drying cycles due to uncertainties of natural rainfall or to intermittent drainage of flooded rice fields during growing seasons (Patrick and Mahapatra,

1968). Therefore, understanding the processes of S and N mineralization under flooded as well as under alternate wetting and drying is very important with respect to S and N availability to rice plants.

Since all biochemical processes in soils are performed by living organisms, enzyme activities in soils play an important role in S mineralization. Among the many enzymes, arylsulfatase is related to S mineralization (Freney, 1967) because it is thought to be important in releasing SO_4 to soil solution. The viable microbial biomass plays an important role in nutrient dynamics in soils. Although microbial biomass S contains only a small fraction (two to three % total soil S) of soil S (Saggar et al., 1981), this fraction is critical for S turnover and transformations in soils (Biederbeck, 1978).

Virtually no information is available on the transformations and distribution of S fractions in relation to soil biological parameters in flooded soils (Freney, 1986). Therefore, this study was undertaken to assess the effect of C:S ratios of organic residues on the transformations of organic S in wetland rice soil under continuous flooding or aerobic-flooding cycles.

MATERIALS AND METHODS

The soil used was a Joydebpur surface soil (0-15 cm) selected to represent a large and intensive rice growing area of Bangladesh. The details of sample preparation and chemical and physical properties of the Joydebpur soil, chemical

analyses of the wheat straw used in the incubation study and analytical procedures were reported in Chapter I.

Incubation Procedure

Details of the incubation procedure were reported in Chapter I. A lab incubation study with a 3 x 2 factorial design (three replications) with three levels of wheat straw added to soil [straw with C:S ratio of 400:1 or 100:1 (25 mg g⁻¹ soil) or control] and two moisture levels [continuous flooding or aerobic (75% of field capacity)-flooding cycles].

The desired C:S ratio of the wheat straw was obtained by growing Stephen wheat in the greenhouse with varying ratios of S which resulted in wheat tissue having C:S ratios of 400:1 (C:S₄₀₀) or 100:1 (C:S₁₀₀).

Thirty g of air-dried soil (2 mm sieved) was mixed thoroughly with wheat straw and transferred into Pyrex tubes. Soils in the tubes were incubated at 35°C as aerobic (75% of field capacity) or flooded (50 ml deionized water (DI) per tube).

At two week intervals for 12 weeks soils in the tubes were destructively sampled and analyzed for NO₃-N, NH₄-N, biomass-S, arylsulfatase activity, reduced S, HI reducible S, C-bonded S, total S and moisture content of the soils. Flood water was also analyzed for NO₃-N, NH₄-N and SO₄-S content.

Analytical Procedure

Details of the analytical procedure were reported in Chapter I. The pH and Eh of the flooded soil were measured directly in the leaching tube using combina-

tion glass electrode and combination platinum electrodes, respectively. Flood water was analyzed for $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ by a Dionex ion chromatograph and $\text{NH}_4\text{-N}$ by steam distillation (Bremner and Keeney, 1965). Moisture content of soil samples were measured using microwave radiation (Hankin and Sawhney, 1978). Microbial biomass S was determined by the chloroform fumigation method (Saggar et al., 1981) which involved a 24 hour chloroform fumigation followed by direct microbial S extraction with 500 mg $\text{Ca}(\text{H}_2\text{PO}_4)_2\text{-P L}^{-1}$ solution. The extracts were obtained by reduced pressure filtration with a 0.45 micron filter, dried in a convection oven and analyzed for total S by alkaline oxidation method of Tabatabai and Bremner (1970a). The biomass S data are reported directly without any conversion by a correction K value.

RESULTS AND DISCUSSION

pH and Eh of Soil Under Continuous Flooding

Figures 7.1 and 7.2 show the effect of added organic residues on the changes in soil pH and Eh respectively, with time of flooded incubation. The pH values of the soil increased rapidly in the first two weeks of flooding, followed by a slower increase up to four weeks, and ultimately stabilizing at a pH of 7.45 to 7.65. The results were in close agreement with Ponnampereuma (1977). Addition of organic residues to soil under flooded conditions did not show any significant effect on soil pH.

With time of flooding, soil Eh decreased dramatically. At two weeks of flooding soil Eh dropped to -262 mV from an initial (time zero) Eh value of +291 mV. At 12 weeks the average soil Eh values were -272 mV. Eh values of +200 to -400 mV are typical for submerged soil and sediments (Ponnamperuma, 1972). Low Eh and neutral pH in flooded soil enhance SO_4 reduction (Ponnamperuma, 1977).

Microbial Biomass S in Soil

Microbial biomass S in chloroform fumigated soils under continuous flooding or aerobic-flooding incubation are shown in Figure 7.3. Among the straw residue treatments, organic residues with straw C:S ratio (100:1) produced significantly higher biomass S than the control or the wide C:S ratio straw (400:1) in both continuous flooding or aerobic-flooding cycles. In addition, aerobic condition enhanced biomass S production, followed by sharp decrease with the onset of flooding. Biomass S under continuous flooding or aerobic flooding cycles showed a significant correlation with all fractions in soil (Tables 7.2 and 7.3).

Microbial biomass S in organic residue treatments with a wide C:S ratio (400:1) under both continuous flooding or aerobic-flooding cycles was consistently low. Results from Chapter IV showed that organic residue with wide C:S ratio (400:1) treatments had low S and C mineralization rates and a low potentially mineralizable S pool under different aerobic-flooding cycles. These results show that a wide C:S ratio organic residue appeared to inhibit microbial biomass because

S was limiting microbial growth which in turn reduced the potential to mineralize organic S.

Arylsulfatase Activity in Soils

The effect of soil organic residue amendments on arylsulfatase activity in soil under continuous flooding or aerobic-flooding cycles are shown in Figure 7.4. Except for the narrow C:S ratio (100:1) treatment under continuous flooding, the arylsulfatase activity under both continuous flooding or aerobic flooding increased up to four weeks followed by a sharp decrease the remaining eight weeks of incubation. In aerobic-flooding cycles, drying the soil to 75% of field capacity at eight weeks followed by aerobic incubation failed to increase the arylsulfatase activity. Reduced arylsulfatase activity was also reported by Cooper (1972) in Northern Nigerian soils due to several wetting-drying cycles.

The correlation matrix in Table 7.2 showed that under continuous flooding arylsulfatase activity is significantly correlated with C-bonded S, ester S, total S, residual S, and flood water SO_4 content of the soil. Conversely, under aerobic-flooding cycles arylsulfatase activity showed a highly significant relationship with biomass S, reduced S, C-bonded S, ester S, residual S, flood water SO_4 and extractable SO_4 content of the soil (Table 7.3).

Reduced S in Soil

Reduced S measured in the soil by zinc-hydrochloric acid distillation method gave quantitative recovery of elemental S, sulfide and thiosulfate, and partial

of other reduced forms of inorganic S (Aspiras et al., 1972). The effect of organic residues on the production of reduced S in soil under continuous flooding or aerobic flooding cycles is shown in Figure 7.5. Reduced S was most pronounced in soil under continuous flooding condition. Irrespective of the treatments, the reduced S in soil was 47 to 84% greater under continuous flooding than under aerobic-flooding cycles. Reduced S was significantly higher in residue treated soils than the control. Abd-el-Malek and Rizk (1963) and Connell and Patrick (1968) observed that sulfide accumulation in wetland soil is promoted by the addition of organic matter.

Higher amounts of reduced S in residue treatments may partially be due to the direct anaerobic reduction of plant S to H_2S . Freney (1967) and Stevenson (1986) have reported that C-bonded S compounds such as cysteine can be directly converted to sulfide. Production of reduced S under flooded condition has also been attributed to: biological reduction of inorganic sulfate to sulfide by respiratory sulfate reduction (Ponnamperuma, 1972). Under flooded condition Eh values were less than -200 mV which was below the critical level of -150 mV for reduction of SO_4 (Connell and Patrick, 1968). Thus conditions in this experiment were conducive for reduction of SO_4 to sulfide. Except for residual S, reduced S in soil was significantly correlated with different S fractions of soil (Tables 7.2 and 7.3).

Ester SO₄ in Soil

Ester SO₄ was determined by difference as follows: Ester SO₄-S = HI-reducible S minus extractable SO₄-S. Figure 7.6 shows the effect of organic residues on the changes in ester SO₄ in soil under continuous flooding or aerobic flooding cycles. Organic residues with a narrow C:S ratio (100:1) produced more ester SO₄ in soil under both continuous flooding or aerobic-flooding cycles. However, compared to continuous flooding, aerobic-flooding cycles had significantly lower levels of ester SO₄ in the soil. The low amounts and decrease of ester SO₄ under aerobic-flooding conditions appears to be the result of increased mineralization from this S pool. Evidence for this is shown in Figure 7.9 where this treatment had elevated levels of SO₄.

Correlations of ester S with various soil properties showed that under both continuous flooding or aerobic-flooding cycles, ester SO₄ was significantly correlated with total S and extractable S content of the soil (Tables 7.2 and 7.3).

C-Bonded S in Soil

Under both continuous flooding or aerobic flooding cycle, the C-bonded S in soils decreased considerably with time of incubation (Fig. 7.7). Since a large portion of C-bonded S is thought to be of amino acid origin (Freney, 1986), the conditions of these treatments favored depletion of this pool. Additionally, micro-organisms in seeking C as an energy source may be mineralizing C-bonded S compounds and simultaneously released S. In both continuous flooding or aerobic

flooding cycles C-bonded S showed a significant correlation with residual S, flood water SO_4 and extractable SO_4 (Tables 7.2 and 7.3).

Residual S in Soil

Residual S was determined by difference as follows:

$$\text{Residual S} = \text{Total S} - \text{HI reducible S} - \text{C-bonded S} - \text{Reduced S.}$$

Under both continuous flooding or aerobic-flooding cycles residual S fraction increased considerably with time of incubation (Figure 7.8) which was probably due to formation of more complex organic S in soil during organic residue decomposition process. The increase was more pronounced in soil under aerobic-flooding cycles (Table 7.4). Correlations in Table 7.2 and 7.3 showed that residual S under continuous flooding and aerobic-flooding cycles were significantly correlated with extractable SO_4 and flood water SO_4 , respectively.

Production of SO_4 -S in Soil

Figure 7.9 shows the effect of organic residue on the production of SO_4 (floodwater plus extractable) in soil under continuous flooding or aerobic-flooding cycles. Under continuous flooding, SO_4 content decreased with time of flooding with an initial value of about $8.85 \text{ mg S kg}^{-1}$ soil to an average value of $4.24 \text{ mg S kg}^{-1}$ soil at 12 weeks of flooding (53% decrease). Low availability of S under flooded conditions has been related to neutral pH (Figure 7.1), and low Eh (Fig. 7.2) which enhances SO_4 reduction (Ponnamperuma, 1972). Sulfate content in the soil under aerobic-flooding cycle was several times higher than under continuous

flooding condition. After 12 weeks of aerobic-flooding cycles there was 4 to 8 times more $\text{SO}_4\text{-S}$ than under continuous flooding. This is consistent with results reported in Chapter I where there were lower S values in soils under flooded condition.

Total S in Soil

Figure 7.10 shows the effect of added organic residues on soil total S content under continuous flooding or aerobic-flooding cycles. Under both continuous flooding or aerobic flooding cycles soil total S content did not change significantly with time of incubation. Freney and Boonjawat (1983) reported that several volatile organic S compounds may be released from flooded soils. Sulfur gases detected in significant amounts were carbon disulfide, carbonyl sulfide, methyl mercaptan, dimethyl sulfide and dimethyldisulfide. But soil total S values after 12 weeks incubation (Table 7.4) showed approximately a 100% recovery of total S when initial total plant S input is included in the estimation (Table 7.1). High recovery of total S in soil implies very little or no loss of S due to volatilization from this experiment.

Hydrogen sulfide (H_2S) produced in flooded soils as a result of SO_4 reduction or protein decomposition. However, the concentration of water soluble H_2S seems to be extremely low under most conditions due to its reaction with ferrous iron or other cations to form insoluble sulfides (Connell and Patrick, 1969; Ponnampereuma, 1977).

Production of NH_4 in Soil

The effect of organic residue on the production of NH_4 (flood water + extractable) under continuous flooding or aerobic-flooding cycles is shown in Figure 7.11. Under continuous flooding organic residues produced significantly greater amounts of NH_4 than the control. The NH_4 concentration was at a maximum after two weeks of flooding. Soils high in organic matter rapidly release NH_4 and attain concentrations exceeding $300 \text{ mg NH}_4\text{-N kg}^{-1}$ soil within two weeks after submergence at 25 to 35°C (Ponnamperuma, 1977). Aerobic-flooding cycles failed to produce a significant amount of NH_4 with time of incubation. This probably differs from continuous flooding because nitrification is inhibited under continuous flooding conditions (Patrick and Mahapatra, 1968) whereas with periodic episodes of aerobic conditions there is an opportunity for nitrification to occur and convert mineralized NH_4 to NO_3 . Nitrate thus produced in the oxidized layer of flooded soil or in aerobic-flooded cycles can easily move downward by diffusion and percolation into the underlying reduced layer, where it is rapidly denitrified (Patrick and Mahapatra, 1965).

Production of NO_3 in Soil

The effect of organic residue on the production of NO_3 (flood water plus extractable) under continuous flooding or aerobic flooding cycles are shown in Figure 7.12. Nitrate concentration in the soil was negligible under continuous flooding conditions. Under aerobic-flooding conditions, straw treated soil produced significantly higher NO_3 concentrations compared to control treatment. Returning

to aerobic conditions after four weeks flooding returned the NO_3 concentration to previous aerobic levels. Very low NO_3 concentration in flooded soil was likely due to the denitrification of NO_3 by aerobic or facultative aerobic microorganism. Low Eh (Figure 7.2) in flooded soil enhances NO_3 reduction (Ponnamperuma, 1977). Higher NO_3 production in the aerobic-flooding cycles may undergo rapid denitrification due to reflooding (Patrick and Mahapatra, 1968).

Distribution and Net Gain or Loss of S Fraction

Initial S fractions in soil and organic residue treatments and distribution of S fraction in soil treated with organic residues at 12 weeks incubation under continuous flooding or aerobic flooding cycles are shown in Tables 7.1 and 7.4, respectively. Net gain or loss of each S fraction (expressed as percent of the total S) after 12 weeks incubation under both flooding or aerobic-flooding conditions is shown in Table 7.5. Results showed that at 12 weeks continuous flooding, plant residue S fraction specially C bonded S and residual S was largely converted to ester S and reduced S. Conversely, under aerobic-flooding cycle residual S and SO_4 -S fraction increased at the expense of ester SO_4 and C-bonded S.

Compared to control or wide C:S ratio (400:1) of the straw treatments, narrow C:S ratio (100:1) treatment produced highest amount of reduced S and ester S in soil (Tables. 7.4 and 7.5) under continuous flooding. Higher amounts of reduced S were due primarily to the reduction of SO_4 to sulfide (Ponnamperuma, 1972), and partially to direct anaerobic reduction of plant S to H_2S (Freney, 1967

and Stevenson, 1986). The high ester S accumulation in soil may be due to lower arylsulfatase activity to hydrolyse ester S to SO_4 form (Figure. 7.4).

Under aerobic-flooding cycles mineralization of SO_4 in wide C:S ratio (400:1) treated soil was lower compared to control or narrow C:S ratio (100:1) treatments (Tables. 7.4 and 7.5). The lower mineralization of SO_4 was considered to be associated with higher immobilization of S, since wider C:S ratio (>400:1) of the organic residues favors immobilization of S (Barrow, 1960).

CONCLUSIONS

The pH values of the soil increased markedly at two weeks of flooding followed by a slower increase up to four weeks and stable pH values attained several weeks of flooding ranges from 7.45 to 7.65 at 12 weeks flooding. At two weeks of flooding soil Eh dropped down to -262 mV from an average initial (week zero) Eh value of +291 mV.

Microbial biomass S at 12 weeks in narrow C:S ratio treated soil under aerobic-flooding cycle produced twice the biomass S as continuous flooding. Except for the narrow C:S ratio (100:1), treatment under continuous flooding, the arylsulfatase activity under both continuous flooding or aerobic-flooding increased up to four weeks, followed by a sharp decrease the remaining eight weeks.

Compared to aerobic-flooding cycles, reduced S was more pronounced in soil under continuous flooding. Irrespective of the treatments, the reduced S in soil was 47 to 84% greater under continuous flooding than aerobic-flooding cycles.

Organic residues with narrow C:S ratio (100:1) produced more ester $\text{SO}_4\text{-S}$ in the soil in both continuous flooding or aerobic flooding cycles. Compared to continuous flooding, aerobic-flooding cycles had significantly lower esters in the soil.

Under both continuous flooding or aerobic flooding cycles, the C-bonded S in soils decreased but residual S increased with time of incubation. Under continuous flooding for 12 weeks, SO_4 content decreased by 53% from an initial value of $8.85 \text{ mg S kg}^{-1}$ soil whereas aerobic-flooding cycles caused an increase in SO_4 with 4 to 8 times more $\text{SO}_4\text{-S}$ than continuous flooding.

After 12 weeks of continuous flooding, plant residue S was largely converted to ester SO_4 and reduced S. Conversely under an aerobic-flooding cycle, plant S was largely converted to the residual S and $\text{SO}_4\text{-S}$ fractions.

Under continuous flooding, organic residues produced significantly higher amounts of NH_4 over the control, with a maximum concentration at two weeks of flooding. Nitrate concentration in the soil was negligible under continuous flooding. Aerobic-flooding cycles failed to produce a significant amount of NH_4 and during the flooding stage the NO_3 content in the soil was drastically reduced. Converting flooded soil to aerobic conditions resulted in increased NO_3 concentrations equivalent to the levels prior to flooding.

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Table 7.1. Initial S fractions (mg S kg⁻¹) in organic residue treatments.

S fractions	Control [†] (no straw)	Wheat straw [‡]	
		C:S ₄₀₀	C:S ₁₀₀
CaP extractable S [§]	8.85 (6.37)	8.85 (5.51)	8.85 (3.71) [#]
Ester S	44.75 (32.24)	46.25 (28.81)	76.50 (32.07)
Reduced S	2.70 (1.95)	2.82 (1.76)	3.13 (1.31)
C-bonded S	36.25 (26.12)	37.49 (23.35)	37.59 (15.75)
Residual S	46.25 (33.32)	65.14 (40.57)	112.50 (47.16)
Total S	138.80 (100)	160.55 (100)	238.55 (100)

[†]Only soil S fractions.

[‡]Includes both soil and straw S fractions.

[§]Calcium phosphate (100 mg P L⁻¹) extractable S.

[#]Figures in parentheses are S fractions expressed as percentage of total S in soil.

Table 7.2. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation in soil under continuous flooding condition.

Properties	pH	Eh	Aryl S [‡]	Biomass S	Reduced S	C-S [§]	Ester S	Total S	Residual S	F. Water [¶] S	CaP extr. [¶] S
pH	--	-0.95***	-0.30 [*]	-0.39**	0.26 [*]	-0.59***	0.35**	0.22	0.44**	0.55***	-0.55***
Eh		--	0.29 [*]	0.27 [*]	-0.39**	0.45**	-0.43**	-0.36**	-0.43**	-0.47***	0.52***
Aryl S			--	-0.02	-0.11	0.30 [*]	-0.29 [*]	-0.28 [*]	-0.43**	-0.42***	0.14
Biomass S				--	0.57***	0.69***	0.50***	0.67***	-0.27 [*]	-0.32 [*]	0.53***
Reduced S					--	0.38**	0.85***	0.93***	-0.16	0.05	0.37**
C-S						--	0.10	0.35**	-0.59***	-0.39**	0.66***
Ester S							--	0.88***	-0.14	0.21	0.33**
Total S								--	0.02	0.04	0.32**
Residual S									--	0.08	-0.72***
F. Water S										--	0.01
CaP extr. S											--

***Significant at the 0.05, 0.01, and 0.001 probability levels, respectively

[†]n = 63

[‡]Aryl S = Arylsulfatase activity

[§]C-S = C-bonded S

[¶]F. water S = flood water S

[¶]CaP extr. S = calcium phosphate (100 mg P L⁻¹) extractable

Table 7.3. Matrix of correlation coefficients (r)[†] between various properties measured over a 12 week incubation in soil under aerobic-flooding cycles.

Properties	pH	Eh	Aryl S [‡]	Biomass S	Reduced S	C-S [§]	Ester S	Total S	Residual S	F. Water [¶] S	CaP extr. [¶] S
pH	--	-0.78***	-0.57**	-0.03	0.09	-0.70***	0.21	0.40*	0.56**	0.59***	-0.25
Eh		--	0.53**	0.41*	0.16	0.62***	-0.26	-0.07	-0.21	-0.22	0.49**
Aryl S			--	0.40**	0.34**	0.71***	0.34**	-0.10	-0.66***	-0.62***	0.50***
Biomass S				--	0.66***	0.28*	0.76***	0.74***	0.18	0.74***	0.94***
Reduced S					--	0.26*	0.73***	0.68***	0.16	0.77***	0.70***
C-S						--	0.29*	-0.10	-0.71***	-0.64***	0.41***
Ester S							--	0.76***	0.13	0.54**	0.76***
Total S								--	0.69***	0.93***	0.62***
Residual S									--	0.88***	-0.27
F. Water S										--	0.46*
CaP extr. S											--

***Significant at the 0.05, 0.01, and 0.001 probability levels, respectively

[†]n = 63

[‡]Aryl S = Arylsulfatase activity

[§]C-S = C-bonded S

[¶]F. water S = flood water S

[¶]CaP extr. S = calcium phosphate (100 mg P L⁻¹) extractable

Table 7.4. Distribution of S fraction (mg S kg⁻¹) in soil treated with organic residues at 12 weeks incubation under continuous flooding or aerobic-flooding cycles.

S fractions	Control (no straw)	Wheat straw	
		C:S ₄₀₀	C:S ₁₀₀
Continuous flooding			
SO ₄ -S [†]	3.37 (2.43) [‡]	3.42 (2.16)	5.92 (2.49)
Ester S	58.11 (41.84)	64.56 (40.74)	112.23 (47.29)
Reduced S	3.37 (2.43)	6.08 (3.84)	32.86 (13.85)
C-bonded S	5.35 (3.85)	2.96 (1.87)	10.32 (4.35)
Residual S	68.69 (49.45)	81.44 (51.39)	75.99 (32.02)
Total S	138.89 (100)	158.46 (100)	237.32 (100)
Aerobic-flooding cycles			
SO ₄ -S	21.40 (14.88)	13.07 (8.23)	49.65 (20.92)
Ester S	16.28 (11.32)	34.69 (21.85)	26.95 (11.35)
Reduced S	1.80 (1.25)	1.65 (1.04)	2.85 (1.20)
C-bonded S	10.51 (7.31)	7.23 (4.56)	8.03 (3.38)
Residual S	93.83 (65.24)	102.09 (64.32)	149.88 (63.15)
Total S	143.81 (100)	158.73 (100)	237.36 (100)

[†]Includes flood water SO₄-S and Ca(H₂PO₄)₂ (100 mg P L⁻¹) extractable SO₄-S

[‡]Figures in parentheses are S fractions expressed as percentage of Total S in soil

Table 7.5. Net gain or loss of S (% of total S) within each S fraction of soil treated with organic residues after 12 weeks incubation under continuous flooding or aerobic-flooding cycles.

S Fraction	Gain or loss of S [†]		
	Control	C:S ₄₀₀	C:S ₁₀₀
Continuous flooding %			
SO ₄ -S	-3.94	-3.35	-1.22
Ester S	9.60	11.93	15.22
Reduced S	0.48	2.08	12.54
C-bonded S	-22.27	-21.48	-11.40
Residual S	16.13	10.82	-15.14
Aerobic-flooding cycles %			
SO ₄ -S	8.51	2.72	17.21
Ester S	-20.92	-6.96	-20.72
Reduced S	-0.70	-0.72	-0.11
C-bonded S	-18.81	-18.79	-12.37
Residual S	31.92	23.75	15.99

[†]Net gain or loss of S in S fractions (% of total S) were calculated as follows:

$$\frac{(\text{Twelve weeks S fraction content})}{(\text{Total S at 12 weeks})} - \frac{(\text{Initial S fraction content})}{(\text{Initial Total S})} \times 100$$

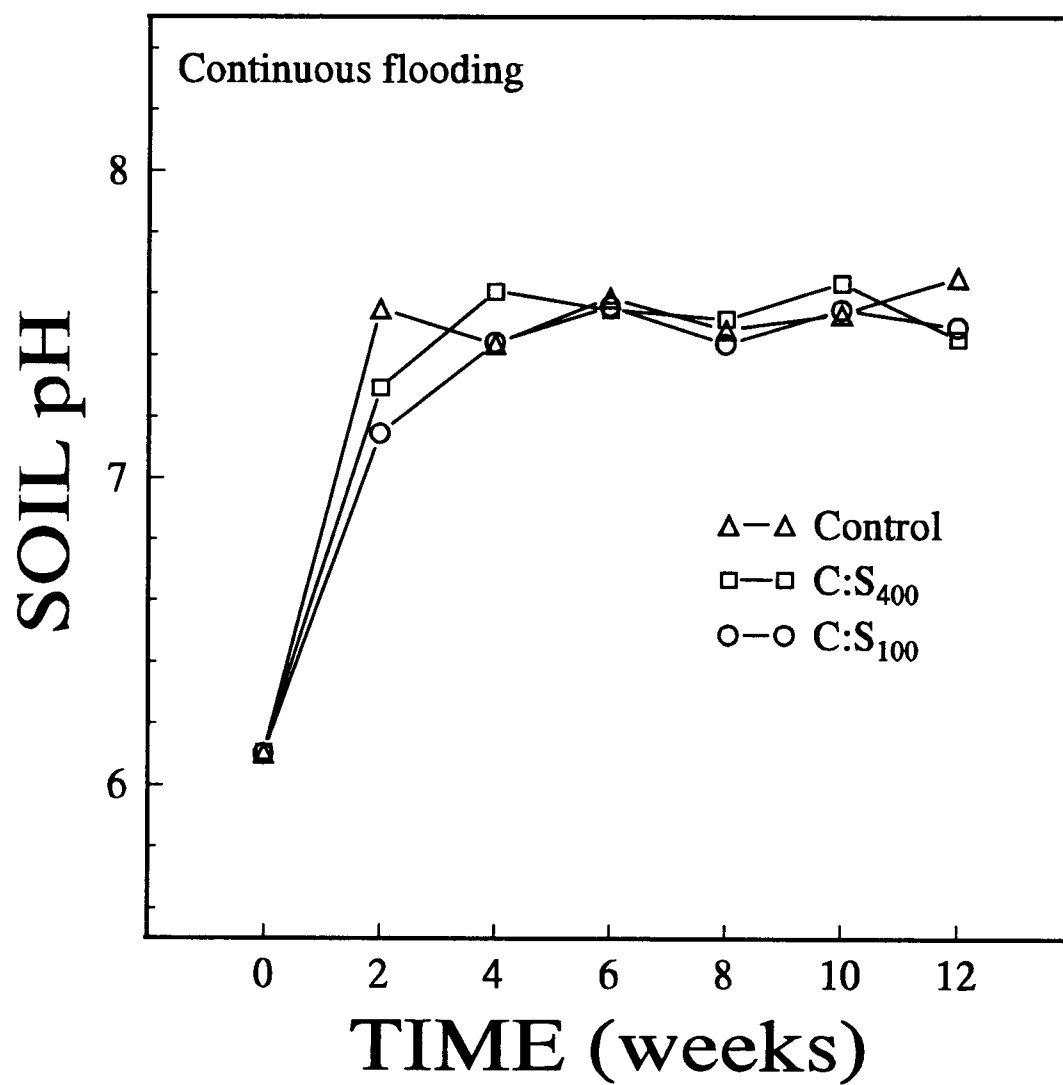


Figure 7.1. Effect of added organic residues on soil pH with time under flooded conditions.

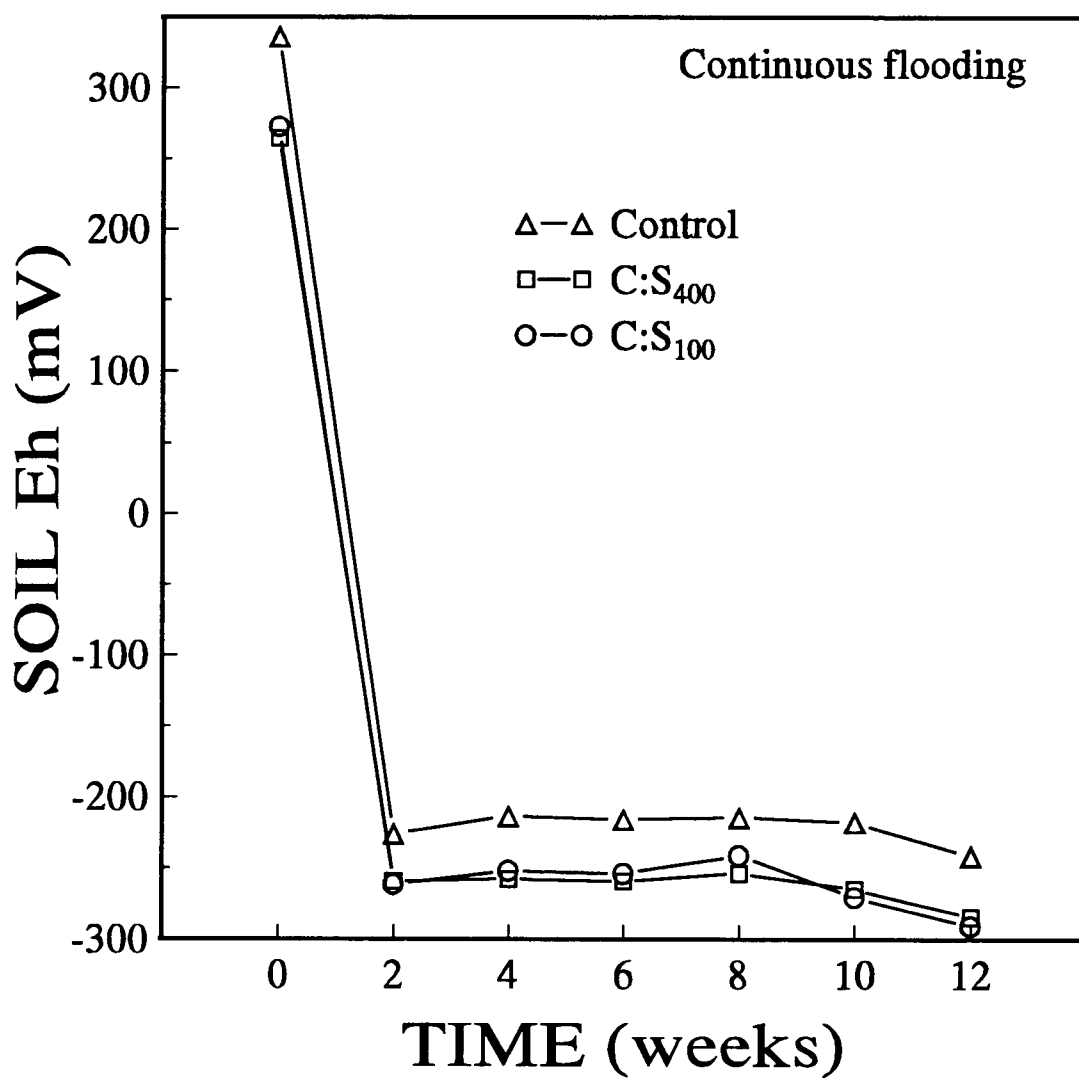


Figure 7.2. Effect of added organic residues on soil redox potential (Eh) with time under flooded conditions.

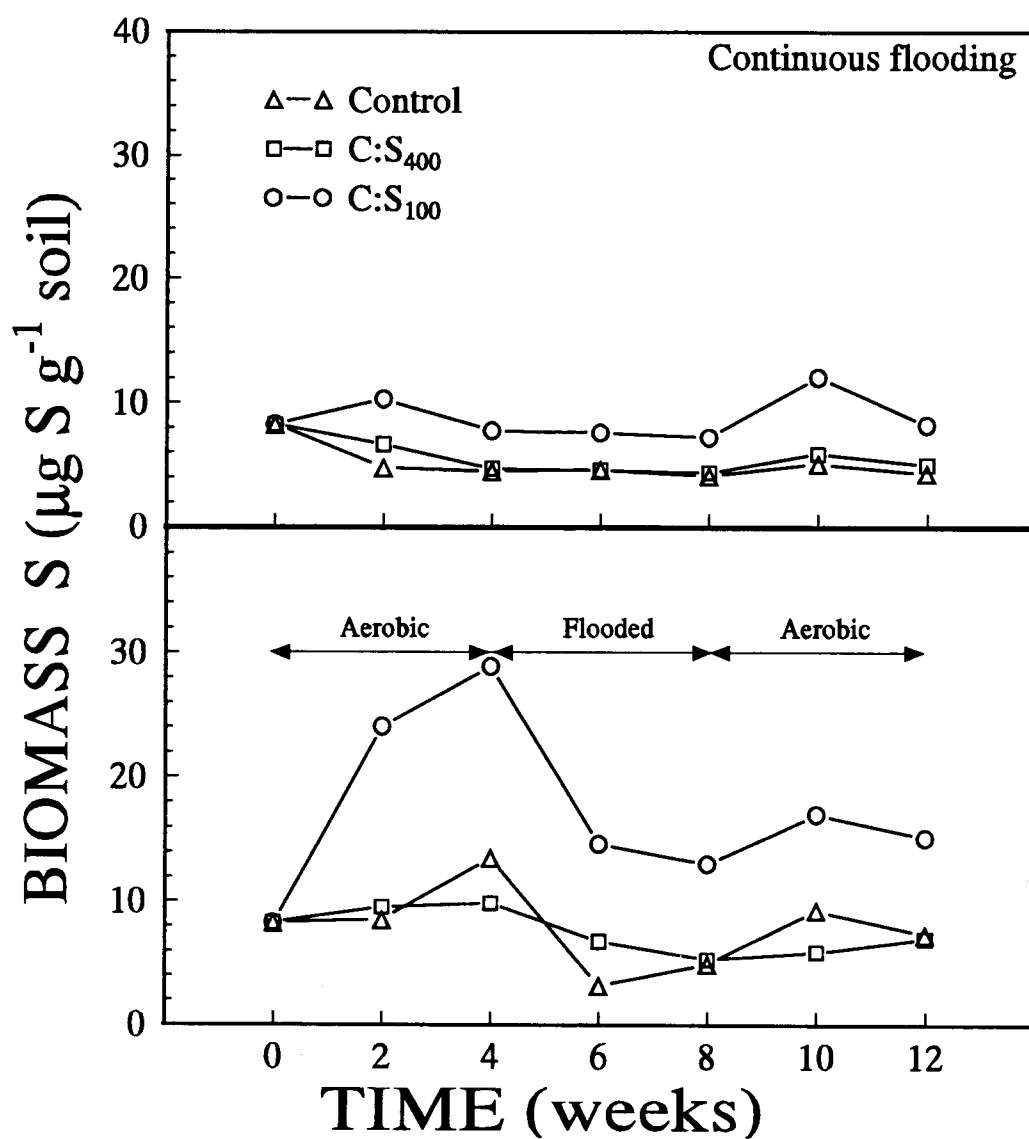


Figure 7.3. Effect of added organic residues on soil microbial biomass under continuous flooding or aerobic-flooding cycles.

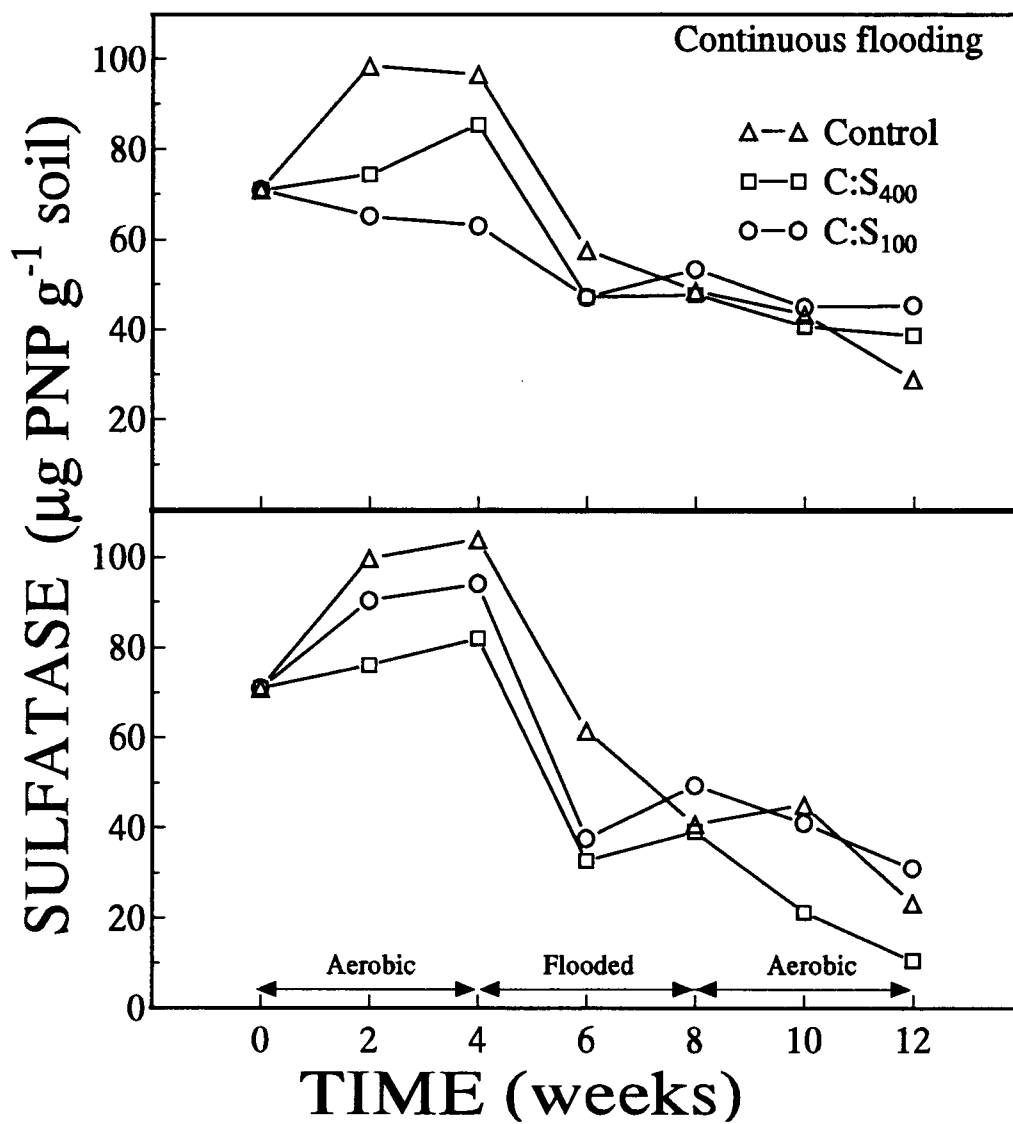


Figure 7.4. Effect of added organic residues on the arylsulfatase activity in soil under continuous flooding or aerobic-flooding cycles.

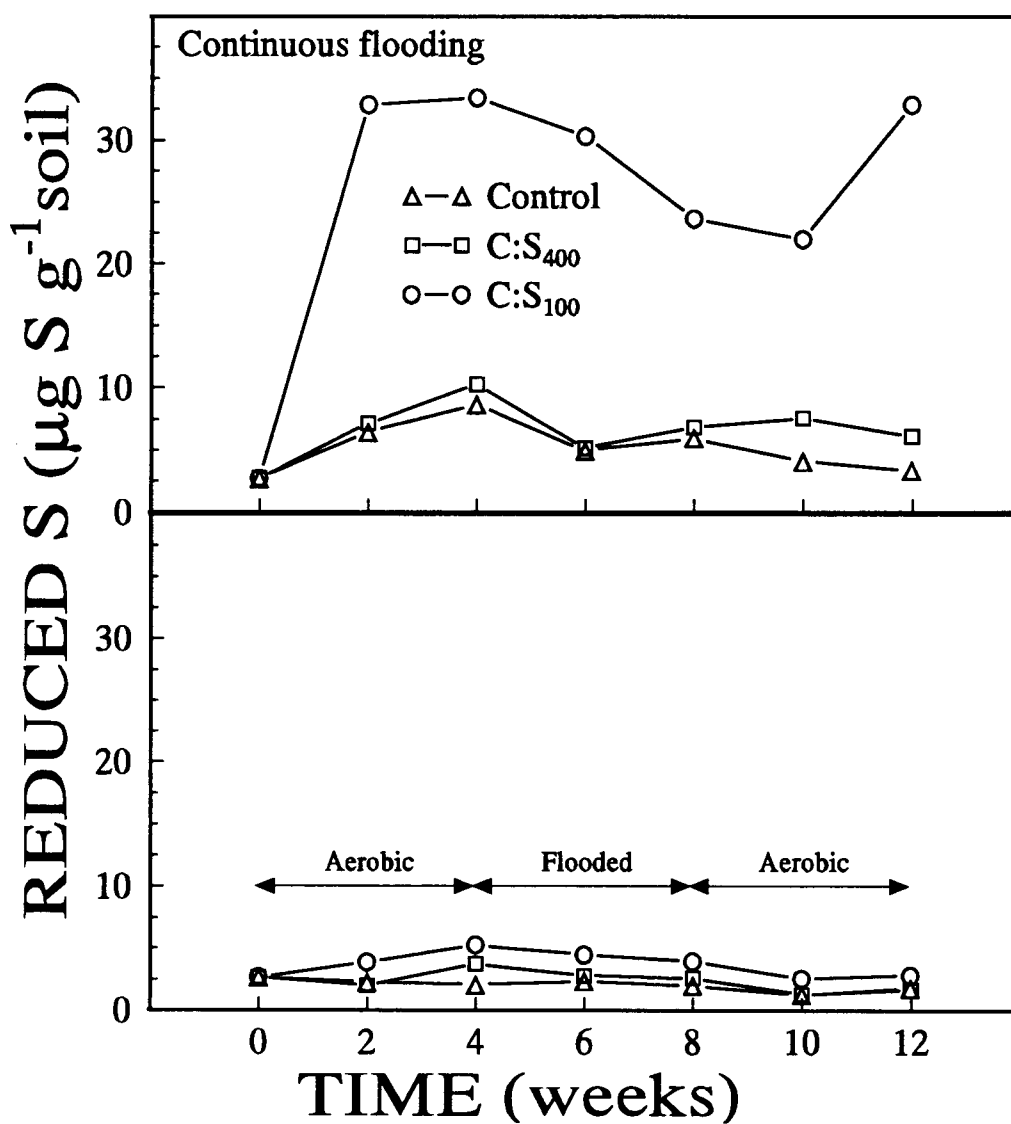


Figure 7.5. Effect of added organic residues on the production of reduced S in soil under continuous flooding or aerobic flooding cycles.

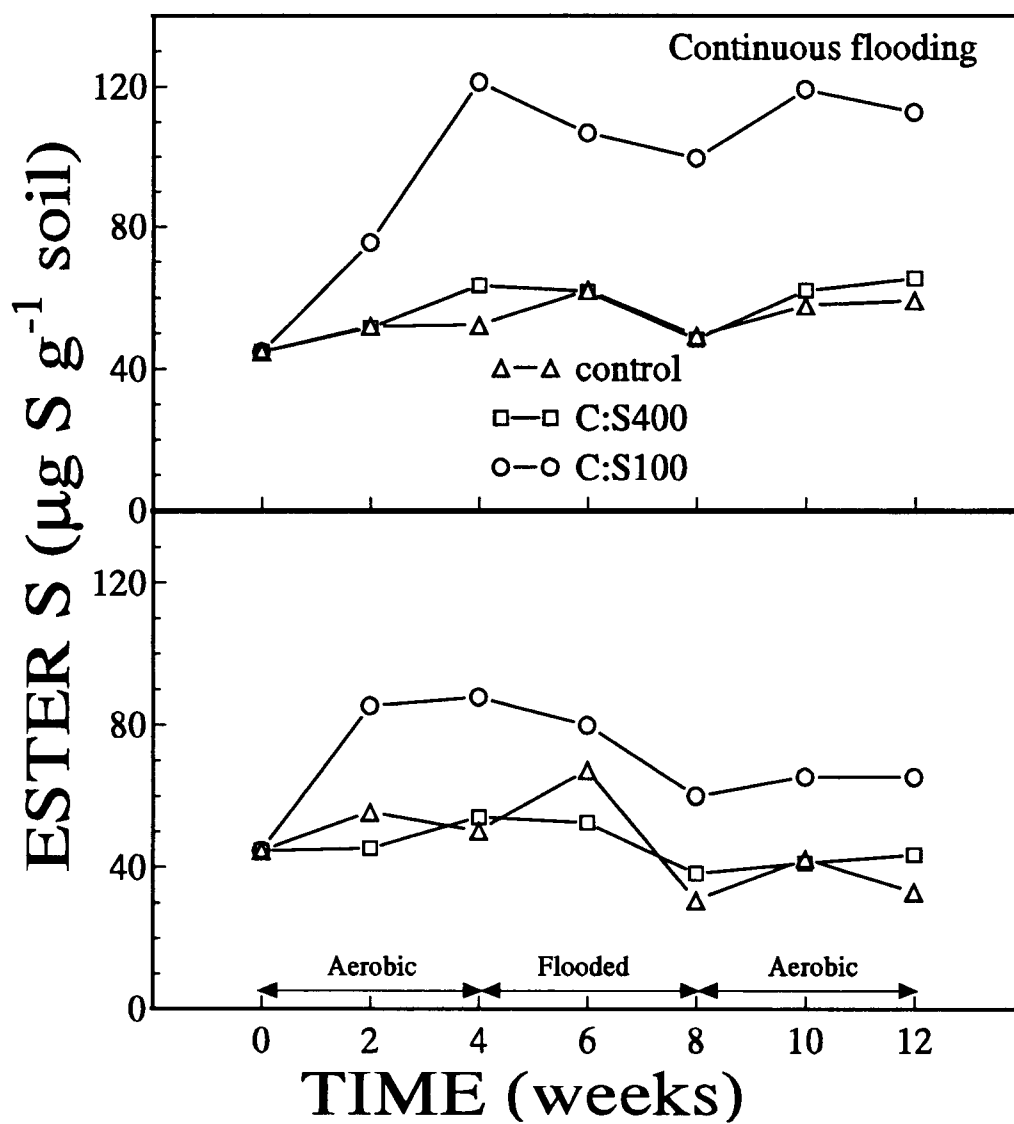


Figure 7.6. Effect of added organic residues on the ester S content in soil under continuous flooding or aerobic- flooding cycles.

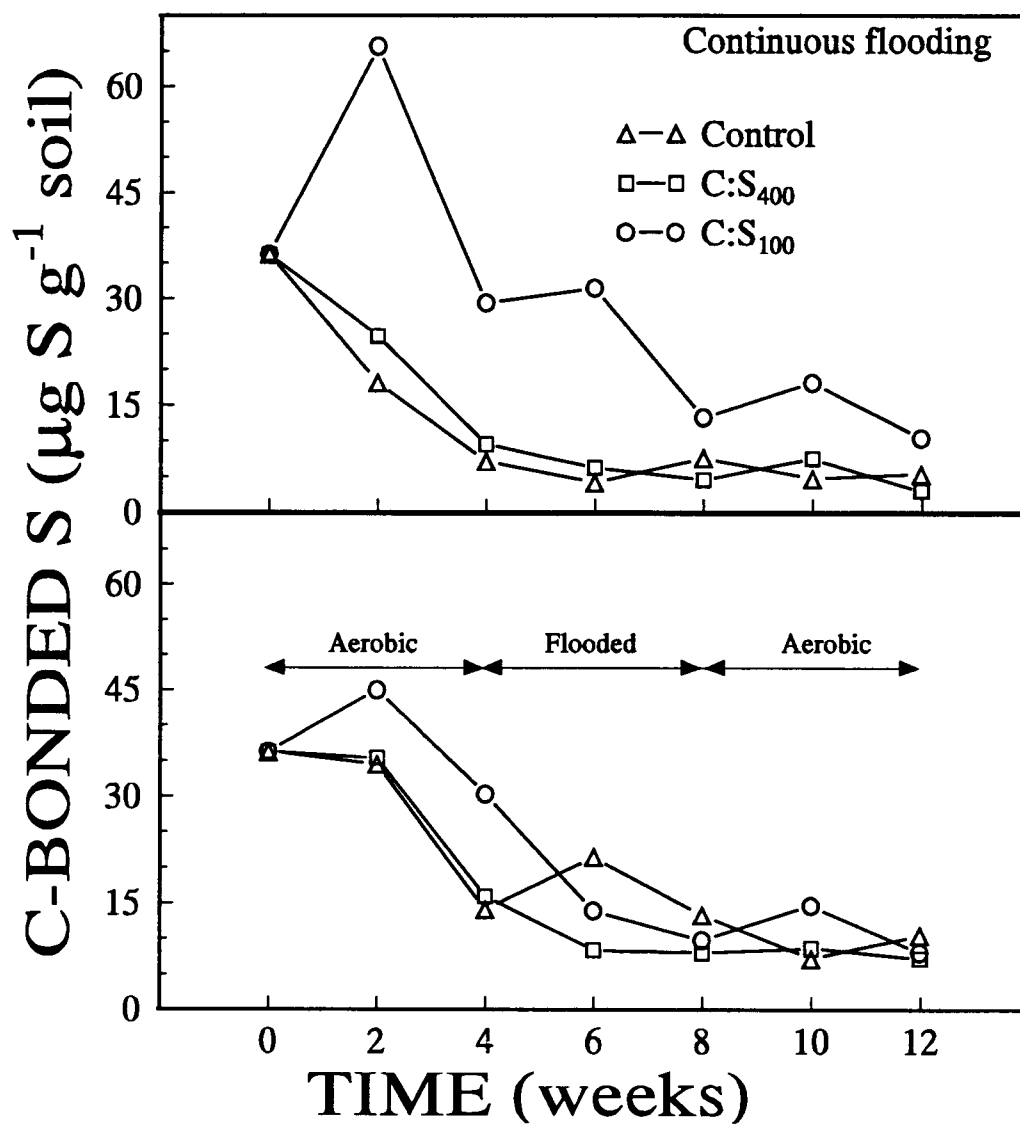


Figure 7.7. Effect of added organic residues on C-bonded S in soil under continuous flooding or aerobic-flooding cycles.

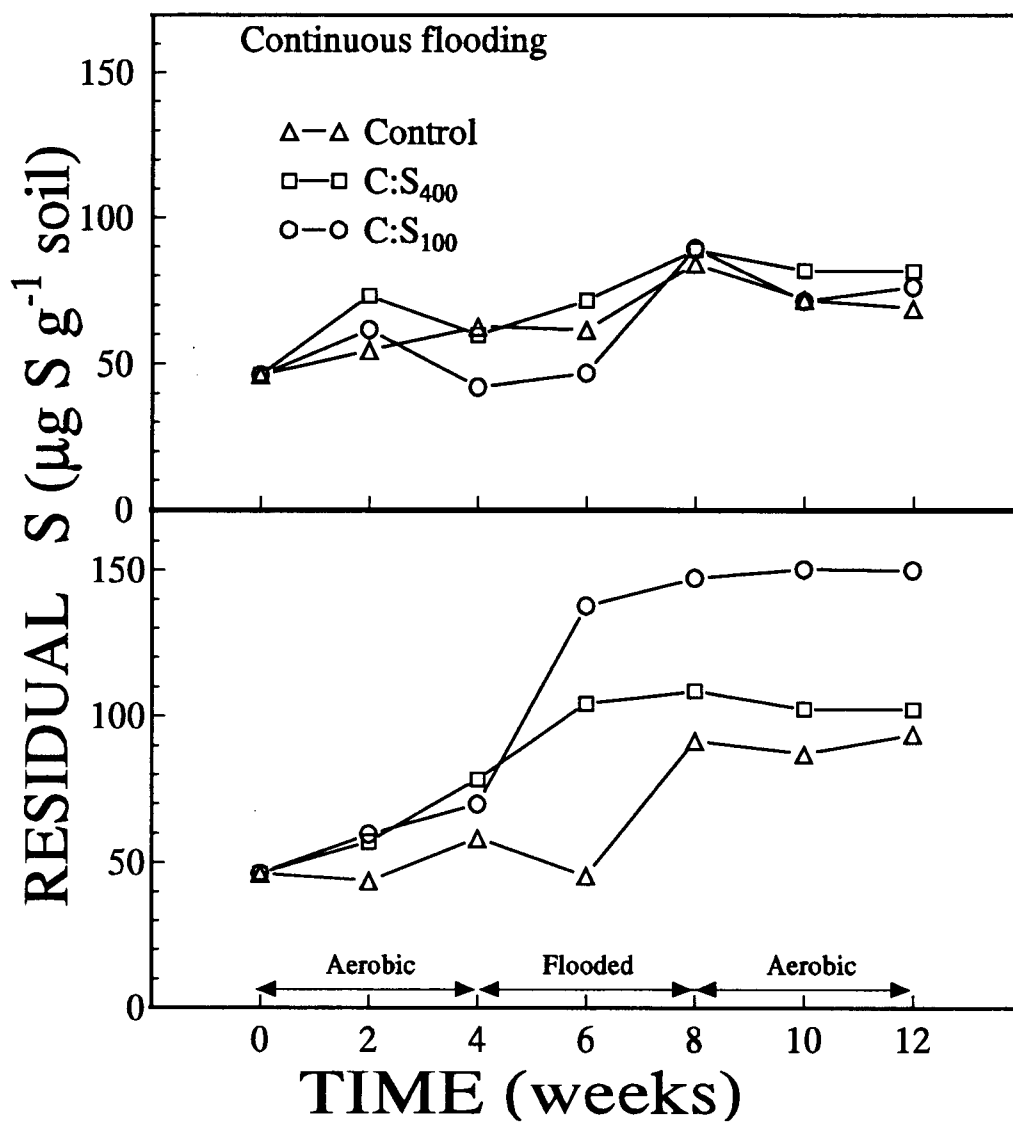


Figure 7.8. Effect of added organic residues on the residual S content in soil under continuous flooding or aerobic-flooding cycles.

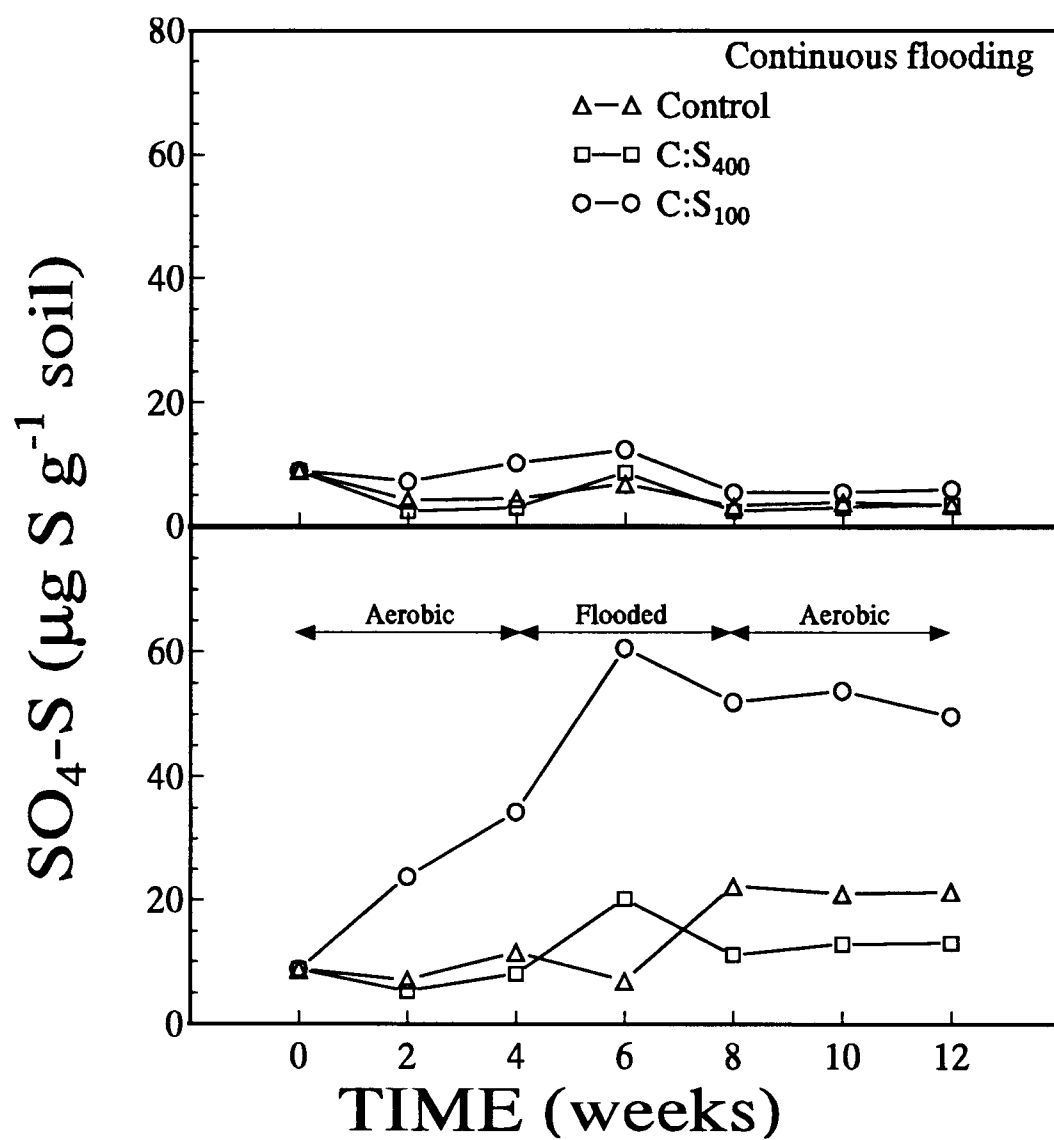


Figure 7.9 Effect of added organic residues on the production of SO₄-S (flood water+extractable) in soil under continuous flooding or aerobic-flooding cycles.

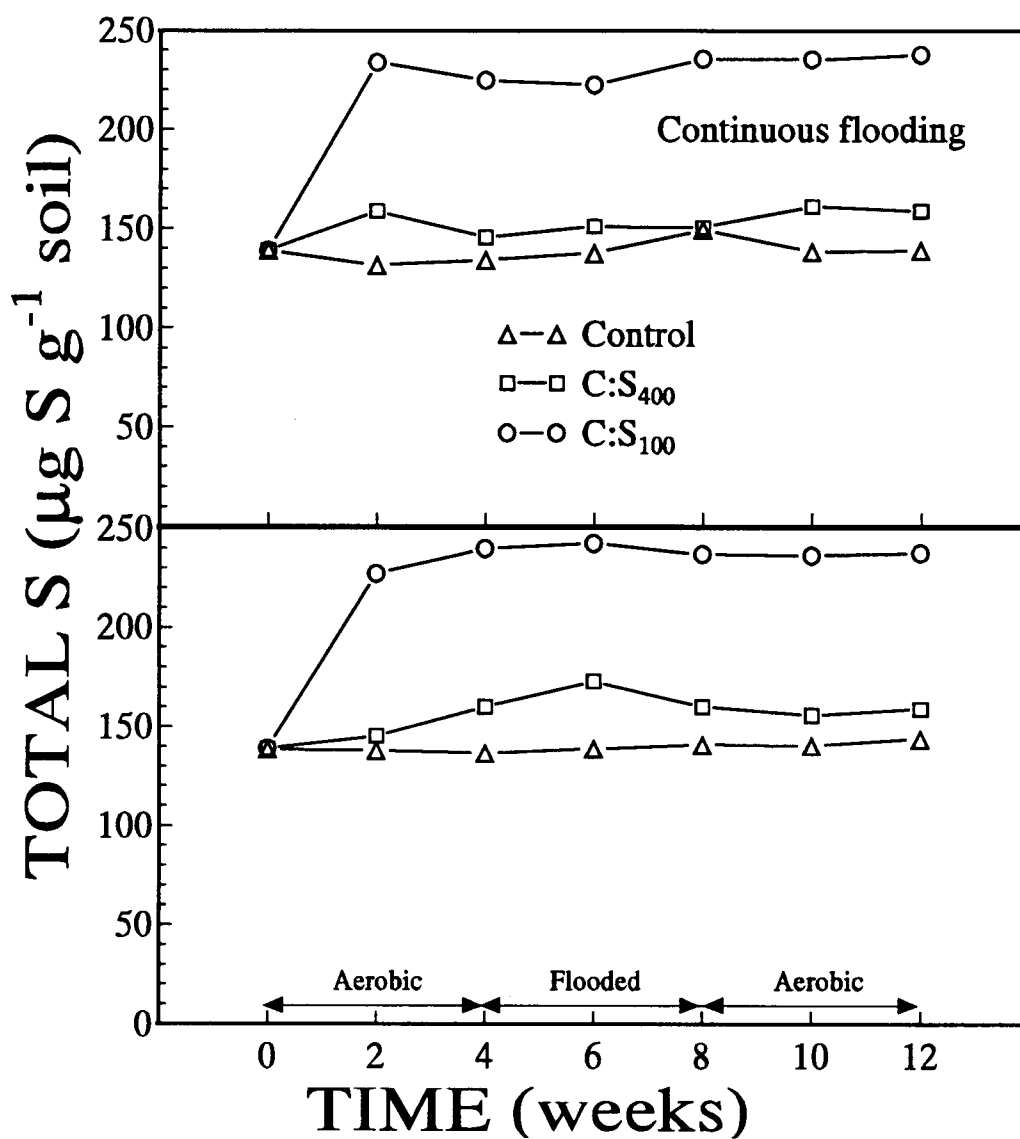


Figure 7.10. Effect of added organic residues on the total S content of the soil under continuous flooding or aerobic-flooding cycles.

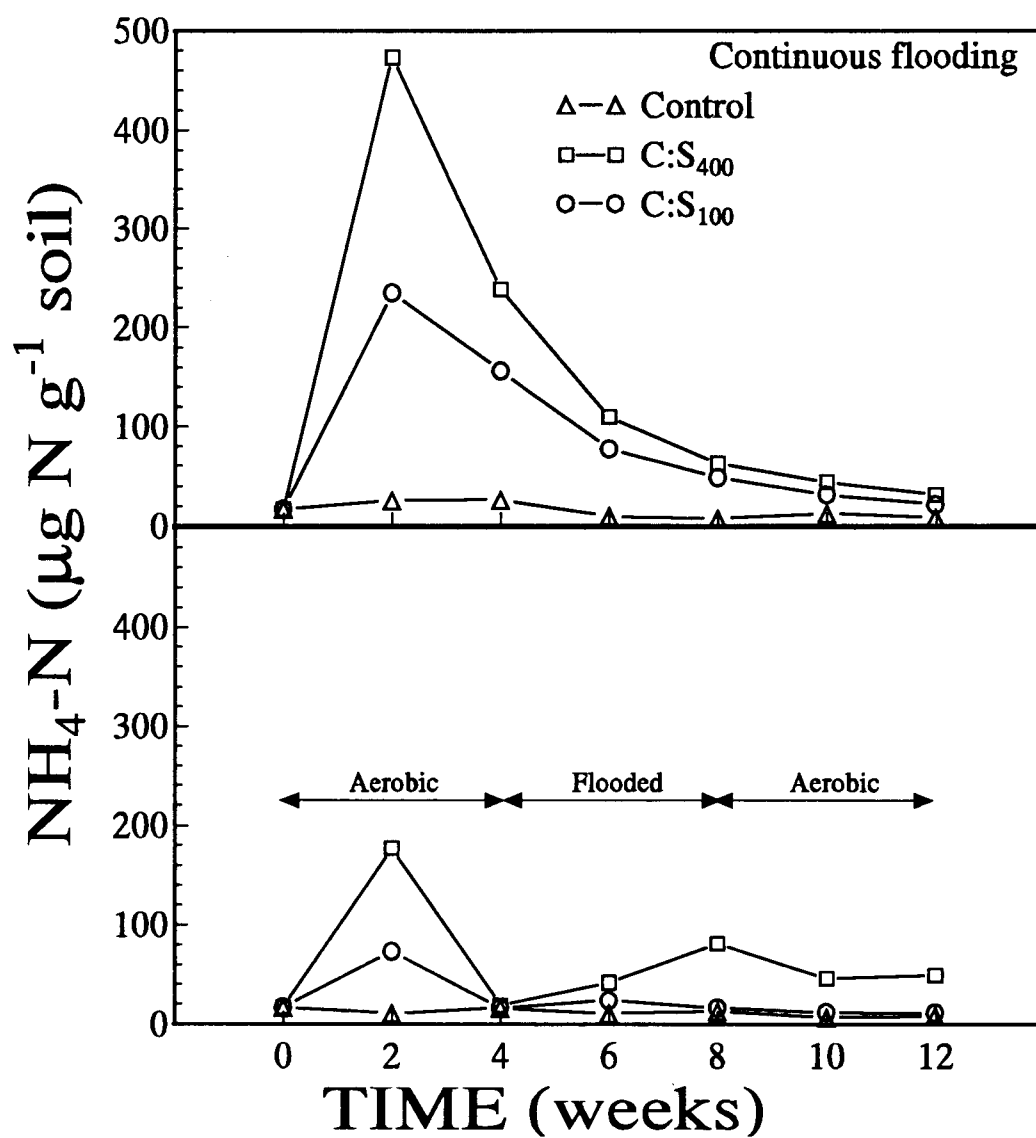


Figure 7.11. Effect of added organic residues on the production of $\text{NH}_4\text{-N}$ (flood water+extractable) in soil under continuous flooding or aerobic-flooding cycles.

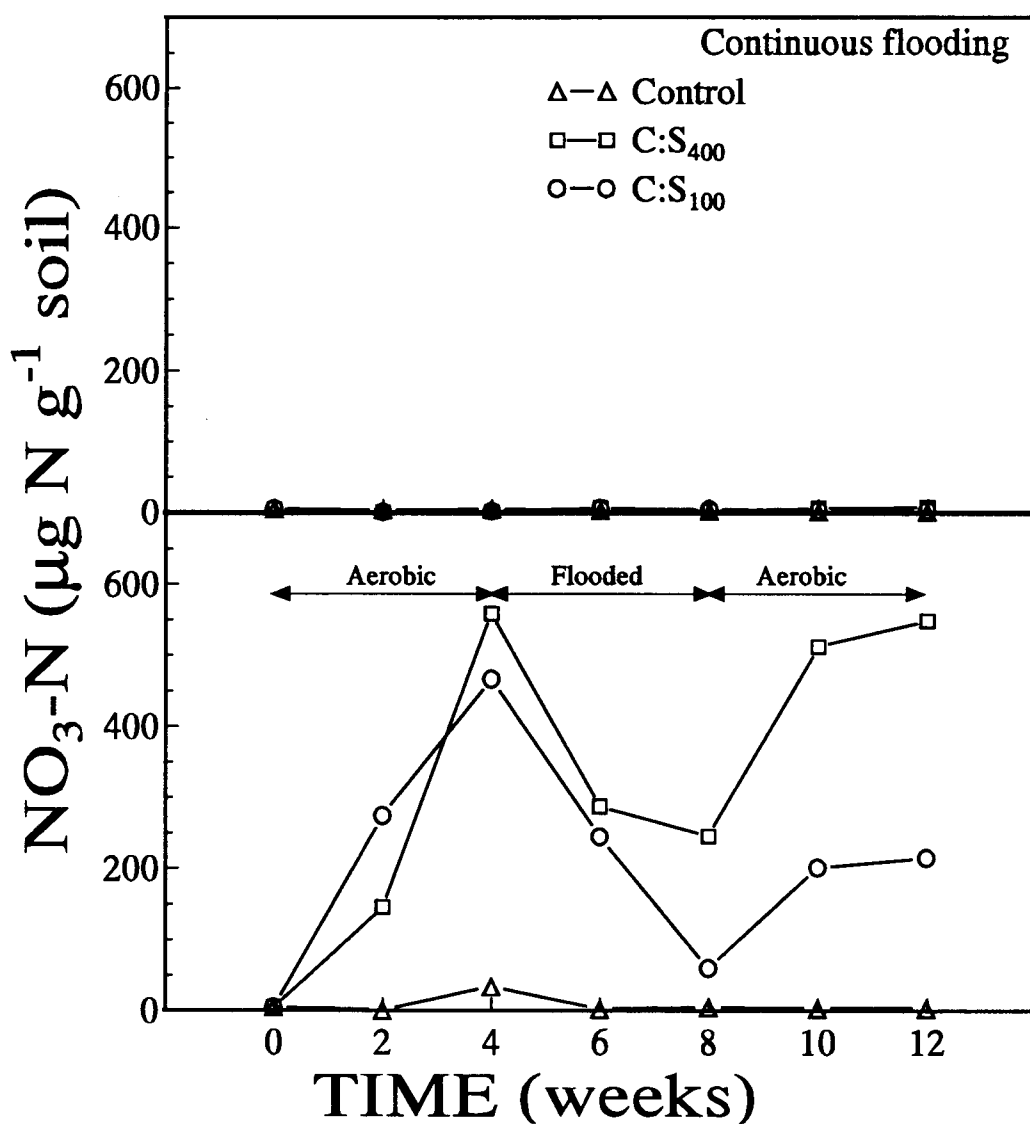


Figure 7.12. Effect of added organic residues on the production of $\text{NO}_3\text{-N}$ (flood water+extractable) in soil under continuous flooding or aerobic-flooding cycles.

SUMMARY AND CONCLUSIONS

In recent years, sulfur (S) deficiency has been recognized as a major constraint to rice production in many tropical areas of the world.

In agricultural soil, organic S is the dominant S fraction and must be mineralized to the inorganic SO_4 to become available for plant uptake. Since rice is grown under flooded conditions, flooding soils creates conditions which markedly affect S transformation. Rice soils are often subject to alternate wetting and drying cycles due to uncertainties of rainfall and management practices. Therefore, understanding the processes of S-transformations under flooded as well as alternate aerobic-flooding cycles are important with respect to S availability to rice plants.

Several incubation studies were undertaken with the objective of determining the effect of organic residues: 1) on the rates of mineralization of S and N, and P release in soils under continuous flooding; 2) with varying C:S ratios on rates of mineralization of S and N, and P release in soils under aerobic-flooding cycles; and 3) on the transformations of organic S fractions in wetland rice soil under continuous flooding or aerobic-flooding cycles.

The findings can be summarized as follows:

1. The potentially mineralizable S pool (S_0) in unamended soils ranged from 14.40 to 24.73 mg S kg^{-1} , whereas the rice straw and pea vine treated soils ranged from 12.18 to 16.14 mg S kg^{-1} and 8.70 to 29.55 mg S kg^{-1} , respectively. The rate constant (K_s) for unamended soils ranged from 0.553 to 0.630 mg S kg^{-1}

wk⁻¹, rice straw and pea vine treated soils ranged from 0.124 to 0.430 and 0.270 to 0.732 mg S kg⁻¹ wk⁻¹, respectively. Except for Thakurgaon soil, the S₀ and K values for the amended Joydebpur and Faridpur soils were lower than the control treatment, indicating poor microbial activity in these soils to mineralize organic S compounds.

The potentially mineralizable N (N₀) in soils amended with rice straw and pea vine were several times greater than the unamended soils. Compared to the control, rice straw had 7 to 15 times and pea vine had 3 to 9 times greater N₀ values in soils. The K_N values for unamended soil ranged from 0.35 to 0.52 mg N kg⁻¹ wk⁻¹ with K_N values for rice straw amended soils being 1.5 to 3.5 times more than the unamended control treatment. Compared to pea vine high N mineralization in rice straw treatment was due to lower C:N ratio (14:1) than wider C:N ratio (30:1) of pea vine.

Cumulative PO₄ released in soils treated with rice straw showed a significantly higher release of PO₄ over pea vine or control treatments. Lower PO₄ released in pea vine treated soils was probably related to the wider C:P ratio (252:1) of pea vine, causing more immobilization of P.

2. Soils treated with narrow C:S ratio (100:1) had significantly higher cumulative SO₄-S over wide C:S ratio (400:1) or control treatment under both two or four weeks aerobic-flooding cycles. Among the two C:S ratios of the straw treatments, S₀ levels were 1.5 to 2 times more in the narrow C:S ratio (100:1) than the wide C:S ratio (400:1) treated soils. The C:S ratio of organic residue did have a significant effect on S mineralization with the narrow C:S ratio (100:1) residue

having average higher K values ($0.127 \text{ mg S kg}^{-1} \text{ wk}^{-1}$) than a wide C:S (400:1) ratio residue ($0.072 \text{ mg S kg}^{-1} \text{ wk}^{-1}$) under aerobic-flooding conditions.

The K_N value for unamended soils was higher than the straw treatments. Lower K_N values in the straw amended soils were due to lower microbial mineralization of organic N compounds. After 12 weeks, four week aerobic-flooding cycles had 1.3 to 2.9 times more mineralized N than two week aerobic-flooding cycles. Low mineralized N in two week aerobic-flooding cycles was probably due to higher denitrification losses of N. N_0 in straw treated soils were 2 to 5.7 times more than the unamended control.

The cumulative amount of PO_4 released in soils amended with organic residues under aerobic-flooding cycles were linear with time of incubation. The slope of the regression equation (rate of P mineralization) in unamended soil ranged from 0.74 to $1.07 \text{ mg P kg}^{-1} \text{ wk}^{-1}$. The slope of the straw amended soils ranged from 0.86 to $1.82 \text{ mg P kg}^{-1} \text{ wk}^{-1}$. Compared to control PO_4 mineralization rates were one to two times more in straw treated soils. The C:S ratio and the frequency of flooding-aerobic cycles (two vs. four week) had a significant effect on P release.

3. Distribution of S fractions (percentage of total S) in soil showed a considerable increase in ester $\text{SO}_4\text{-S}$ and reduced S fraction and decreases in C-bonded S and $\text{SO}_4\text{-S}$ fractions under continuous flooding conditions. Conversely, the $\text{SO}_4\text{-S}$ and residual S fraction were significantly increased in aerobic-flooding cycles with time of incubation. Aerobic-flooding condition provides significantly more plant available $\text{SO}_4\text{-S}$, 4 to 8 times more than under continuous flooding.

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