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Article

Integrated Soil Fertility Management Enhances Soil Properties, Yield, and Nitrogen Use Efficiency of Rice Cultivation: Influence of Fertilizer Rate, Humic Acid, and Gypsum

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Abstract: Integrated soil fertility management is essential to improve soil productivity, rice yield, and nitrogen use efficiency (NUE). This study evaluated the integration of chemical fertilizer rate, humic acid (HA), and flue gas desulfurization gypsum (FG) on soil chemical properties, rice yield, NUE, and nitrogen agronomic efficiency (NAE) in acidic paddy soil. This study included three factors: (1) fertilization based on farmer practices and rice requirements, (2) HA at 0 and 975 kg ha⁻¹, and (3) FG at 0, 636, and 23 kg ha⁻¹. Fertilization based on rice requirements reduced nitrogen (N) input by 14.5% compared to farmer practices while maintaining similar yields. Under farmer practice, HA enhanced total N, CEC, rice yield, NUE, and NAE. HA with FG at 636 kg ha⁻¹ increased TOC, total N, and exchangeable NH₄-N but decreased yield. In contrast, HA combined with FG at 23 kg ha⁻¹ enhanced soil exchangeable Ca and S, rice yield, NUE, and NAE. This study suggests that to maintain farmer fertilization practices while improving soil properties and rice yield, HA should be applied with FG (23 kg ha⁻¹). HA combined with FG (636 kg ha⁻¹) should be applied with fertilization tailored to rice nutrient requirements to optimize NUE and NAE.

Keywords: integrated soil fertility management; humic acid; flue gas desulfurization gypsum; nitrogen use efficiency; agronomic efficiency; acidic paddy soil

1. Introduction

Rice is a staple food and a major contributor to food security, particularly in Asia, where it is not only widely cultivated and consumed but also supports millions of livelihoods [1]. Various nutrient and soil fertility management strategies have been employed to maximize rice yield and enhance fertilizer use efficiency. Generally, farmers in developed countries, such as those in Thailand, commonly rely on conventional nutrient management based on their personal experience, knowledge or perception rather than scientifically informed approaches [2,3]. Consequently, these practices often fail to align with actual crop nutrient requirements, resulting in low nitrogen use efficiency (NUE) and agronomic efficiency (NAE). To exemplify, over-fertilization of N under farmer practices in China (205 N kg ha⁻¹) in late-season rice led to reduce rice yield and lower NUE (22%) and NAE (6 kg kg⁻¹) compared to a nutrient expert system that achieved higher (NUE 33%) and NAE (20 kg kg⁻¹) [4]. This highlights the inefficiency of excessive fertilizer inputs, which contributed to both economic loss and environmental degradation [5]. Low yield and use efficiency of applied fertilizer under farmer practices had presented significant opportunities for improvement in farmer practices to enhance their NUE and NAE. The improvement strategies of NUE and NAE are vital for

sustainable rice production as they increase yield and decrease nutrient inputs which help increase the beneficial returns to farmers.

Aligning fertilizer application to crop nutrients requirements is the key to success in obtaining optimum nutrient application rates and achieving the targeted yield [6]. Previous studies revealed that the fertilizer input in line with crop nutrient requirements achieve targeted yields and optimize NUE in numerous crops, including rice and maize [7,8]. The amounts of nutrients required to attain targeted yield vary among plant species and varieties [9,10]. For instance, producing 1 ton of grain requires approximately 14 kg N ha⁻¹ for Indica hybrid rice and 18 kg N ha⁻¹ for Japonica rice [9]. The study by Sukitprapanon et al. [11] reported that rice in Thailand absorbs about 21 kg N ha⁻¹ per 1 ton of grain produced.

Integrated soil fertility management (ISFM) practice is the integration of inorganic, organic, natural nutrient resources, and agronomic practices to enhance soil fertility and promote crop productivity and sustainability [12]. ISFM has been widely adopted to improve long-term soil health while minimizing environmental impact by reducing chemical fertilizer input [13,14]. Its key components include inorganic fertilizers, organic amendments (e.g., compost, manure, green manure, and cover crops), and locally accessible soil amendments (e.g., biochar, humic acid (HA), gypsum, and lime). In principle, the ISFM incorporates at least two of these components [15]. However, the use of organic amendments as one of the ISFM components possesses a slow onset effect since they initially undergo a decomposition process to produce humic substances [16]. This slow onset effect can be accelerated by adding a pre-made HA into the soil as a soil amendment.

HA is a major component of humic substances formed after the complete decomposition of organic matter. The extraction of HA can be enhanced by sourcing it from various organic materials, which contain the following percentages of HA: sugarcane waste compost (49%), vermicompost (6-8%), farmyard manure (4%), chicken dung compost (5%), sewage sludge (31%), and leonardite (30-56%) [17,18]. Leonardite is mainly used for global HA production because of its natural abundance, cost-effectiveness, high HA contents, and high amounts of plant nutrients, such as N [19]. The HA also supplies additional carbon to promote total organic carbon (TOC) accumulation in soils [20]. In addition, the HA improves soil structure as it plays a role as a binding agent that binds soil particles to form microaggregate that accelerates soil aggregate formation [21]. The HA functional groups, such as carboxylic (R-COOH) and phenolic (R-OH), form complex and chelate more exchangeable cations resulting in enhancing cation exchange capacity (CEC), which is linked to high nutrient retention in soils [22]. The HA has a positive effect on N cycling by enhancing N availability and reducing its loss as HA delays the hydrolysis of ammonium (NH₄⁺) to nitrate (NO₃⁻) [23]. Thereby, HA application has been shown to boost soil nutrient turnover, nutrient uptake, yield, and NUE of crops, such as maize, wheat, and rice [24-26].

Flue gas desulfurization gypsum (FG), a by-product of coal combustion in power plants, is locally accessible, abundant, and cost-effective as a soil amendment. The application of FG can improve extractable calcium (Ca) and sulfur (S) in soils, particularly acidic soils deficient in Ca [27,28]. The Ca released from FG displaces exchangeable bases (e.g., Mg, K and Na) in topsoil, allowing the bases to move downward in the soil profile [29]. The Ca, derived from FG, promotes soil aggregate formation and clay flocculation [30]. In addition, the Ca plays a role in N translocation and enhances NUE in plants [31].

Previous studies showed that coapplication of HA and FG to salt-affected soils positively affected not only soil properties (e.g., electrical conductivity (EC), TOC, water-stable macroaggregate, and available water content), but also the crops yield (e.g., rapeseed and rice) [32-35]. The coapplication HA and FG can achieve better N retention [36]. The incorporation of HA with FG in coastal saline soil improved rice yield by 10%, mitigated greenhouse gas emissions by 32%, and enhanced NUE by 27% [35]. However, the previous studies had not explored the mechanism under the coapplication effect of HA and FG on the N dynamics in acidic paddy soils. In addition, the previous studies have been performed in salt-affected soils, which sodium toxicity is the main

problem. No studies have been conducted on the combined applications of fertilizer, HA, and FG on soil properties, yield, NUE, and NAE in an acidic paddy soil with Ca deficiency as a key problem.

Therefore, this study hypothesized that the interaction effect of soil fertilized based on crop nutrient requirement with HA and an optimal FG rate can effectively increase TOC, CEC, exchangeable forms of $\text{NH}_4\text{-N}$ ($\text{NH}_4\text{-N}$), Ca and S, NUE, and NAE for rice production in an acidic paddy soil. This study aims at (1) determining the application effects of fertilizer, HA, and FG on soil properties, yield, NUE, and NAE, and (2) determining the relationship between rice yield and NUE and rice yield and NAE for rice cultivation in an acidic paddy soil. This study contributes to effective nutrient management practices that enhance rice production while decreasing the use of chemical fertilizers, thus promoting sustainable agriculture and a healthier environment.

2. Materials and Methods

2.1. Site Characteristics

A pot experiment was conducted from August 2022 to January 2023 in a greenhouse at the Soil and Fertilizer Research Station, Khon Kaen University, Khon Kaen, Thailand. The initial soil used in this study was collected from a paddy field in Khon Kaen, Thailand (UTM: 48Q 256751E, 1827796N), topographically 187 m above sea level. The study area was under a tropical savanna climate, with an average maximum temperature of 32°C and a minimum of 21°C. Cumulative precipitation during experiment was 412 mm [37]. The paddy soil used in this study was classified as Aeric Kandiaquult according to Soil Taxonomy [38]. The topsoil (0-15 cm) is sandy loam with sand, silt, and clay contents of 583, 359, and 58 g kg⁻¹, respectively. The initial soil was acidic (pH 4.7) and had low levels of EC (0.08 mS cm⁻¹), TOC (1.6 g kg⁻¹), CEC (2.6 cmol kg⁻¹), exchangeable ammonium nitrogen ($\text{NH}_4\text{-N}$) (23 mg kg⁻¹), exchangeable nitrate nitrogen ($\text{NO}_3\text{-N}$) (12 mg kg⁻¹), exchangeable Ca (95 mg kg⁻¹), and exchangeable S (37 mg kg⁻¹). Additionally, the soil had total N, Ca, and S concentrations of 0.56, 0.28 and 0.14 g kg⁻¹, respectively (Table 1).

Table 1. Characteristics of soil, humic acid, and flue gas desulfurization gypsum used in this study.

Property	Initial soil	Humic acid	FG
Soil classification	Aeric Kandiaquult	-	-
Soil texture	Sandy loam	-	-
Sand (g kg ⁻¹)	583	-	-
Silt (g kg ⁻¹)	359	-	-
Clay (g kg ⁻¹)	58	-	-
pH	4.7	9.8	7.7
EC (mS cm ⁻¹)	0.08	8.3	3.3
TOC (g kg ⁻¹)	1.6	291	-
CEC (cmol kg ⁻¹)	2.6	57	-
$\text{NH}_4\text{-N}$ (mg kg ⁻¹)	23	-	-
$\text{NO}_3\text{-N}$ (mg kg ⁻¹)	12	-	-
Exchangeable Ca (mg kg ⁻¹)	95	-	-
Exchangeable S (mg kg ⁻¹)	37	-	-
Total N (g kg ⁻¹)	0.56	11	0.12
Total Ca (g kg ⁻¹)	0.28	9.4	388
Total S (g kg ⁻¹)	0.14	6.7	199

HA = Humic acid; FG = Flue gas desulfurization gypsum; EC = Electrical conductivity; TOC = Total organic carbon; CEC = Cation exchange capacity; NH₄-N = Exchangeable ammonium nitrogen; NO₃-N = Exchangeable nitrate nitrogen; Total N = Total nitrogen; Total Ca = Total calcium; Total S = Total sulfur.

2.2. Greenhouse Experiment

The experimental design was arranged in 2 × 2 × 3 factorial in a randomized complete block design with three replications. Three factors for the ISFM were employed. The first factor was chemical fertilizer at two application rates, including rates pertaining to farmer practices (F1) and those pertaining to rice nutrient requirements (F2). According to the study by Sukitprapanon et al. [11], the N, P₂O₅, and K₂O nutrient inputs pertaining to F1 were 75, 38, and 38 kg ha⁻¹ and those to F2 were 61, 25, and 12 kg ha⁻¹, respectively. The applied chemical fertilizer was prepared from urea (46-0-0), diammonium phosphate (DAP) (18-46-0), and muriate of potash (MOP) (0-0-60) at the rate of 131, 81, and 63 kg ha⁻¹ for F1 and at the rate of 112, 53, and 19 kg ha⁻¹ for F2, respectively. Compared to the nutrient input based on farmer practices, the chemical fertilizer applied based on rice requirement declined by 14.5, 34.6, and 69.8% for urea, DAP, and MOP, respectively.

The second factor was HA incorporation. The HA used in this study was produced from leonardite, which was obtained from Concurchem Co., LTD, Bang Yai District, Nonthaburi, Thailand. HA was strongly alkaline (pH 9.8) and contained elevated level of EC (8.3 mS cm⁻¹), and elevated contents of TOC (291 g kg⁻¹), CEC (57 cmol kg⁻¹), total N (11 g kg⁻¹), total Ca (9.4 g kg⁻¹), and total S (6.7 g kg⁻¹) (Table 1). The HA applied, including no HA (H0) and with HA applied at the rate of 975 kg ha⁻¹ (H1), which provided the input of 10.68 kg ha⁻¹ of N. This HA application rate was acquired from the optimum rate for rice production in paddy soils in Northeast Thailand found in the previous study by Sukitprapanon et al. [11].

The last factor was FG application rates. The FG used in this study was obtained from Mae Moh Power Plant, Electricity Generating Authority of Thailand, Mae Moh District, Lampang Province, Thailand. The FG used in the study was neutral (pH H₂O 7.7) and rich in total concentrations of Ca (388 g kg⁻¹) and S (199 g kg⁻¹) (Table 1). There were three rates of FG applied: no FG (G0), an application rate based on gypsum requirements (GR) for acidic soil (636 kg ha⁻¹) (G1), and based on the amount of Ca required by rice (23 kg FG ha⁻¹) (G2), which supplied total N to the soil of 0, 0.08, and 0.003 kg ha⁻¹, respectively. The GR was calculated by multiplying the clay content (g kg⁻¹) by 6 and dividing the result by 1000 as suggested by several studies such as [28,39,40], whereas Ca required by rice was suggested by Sukitprapanon et al. [11]. The Ca rice required is 7.9 kg ha⁻¹ for a 1-ton grain ha⁻¹ production Sukitprapanon et al. [11].

The summary of total inputs of N from chemical fertilizer, HA, and FG is shown in Table 2. In this study, three pots without additions of fertilizer, HA, and FG were set aside for the analyses of NUE and NAE. Soil amendments were incorporated and incubated for 14 days before rice transplantation. Half of N and full dose of P₂O₅ and K₂O were applied at 7 days after transplanting, while the remaining half of N was applied at the panicle stage, which was approximately 65 days after planting (DAP).

Table 2. The amounts of nutrient nitrogen input (kg ha⁻¹) from chemical fertilizer, humic acid, and flue gas desulfurization gypsum used in this study.

Treatment	Nitrogen input (kg ha ⁻¹)			
	Fertilizer	HA	FG	Total
F1H0G0	75	0	0	75
F1H0G1	75	0	0.08	75.08
F1H0G2	75	0	0.003	75.003
F1H1G0	75	10.68	0	85.68
F1H1G1	75	10.68	0.08	85.76

F1H1G2	75	10.68	0.003	85.683
F2H0G0	61	0	0	61
F2H0G1	61	0	0.08	61.08
F2H0G2	61	0	0.003	61.003
F2H1G0	61	10.68	0	71.68
F2H1G1	61	10.68	0.08	71.76
F2H1G2	61	10.68	0.003	71.683

HA = Humic acid; FG = Flue gas desulfurization gypsum; F1 = Fertilizer application rate based on farmer practices; F2 = Fertilizer application rate based on rice nutrient requirements; H0 = No HA; H1 = HA application at 975 kg ha⁻¹; G0 = No FG; G1 = FG application rate followed gypsum requirement at 636 kg ha⁻¹; G2 = FG application rate based on Ca required by rice at 23 kg ha⁻¹.

The rice (*Oryza sativa* L.) (Sakon Nakhon variety) was sown in a plastic tray filled with soil. After 14 days, the seedlings that had similar growth were selected and transplanted to a pot with the dimensions of 30 cm length × 30 cm width × 39 cm height at 20-cm spacing. The soil was kept under a waterlogged condition at 5 cm water height above the soil surface from transplanting to 7 days before harvest. Crop management practice, including seed selection, seedling, transplanting, weeding, pest and disease control, and harvesting, followed the Thai Department of Agriculture recommendation [41]. The grain yield, straw, and root biomass from each pot were recorded at harvest (128 DAP). The rice grain, straw, and root were cleaned with deionized water (DI water) and stored in sample paper bags, which were transported to the laboratory. All parts of the rice were oven-dried at 65°C until constant weight. The oven-dried samples were then finely ground using a plant grinder for total N concentration analysis.

2.3. Soil Sampling

Soil samples were collected from the pot after rice was harvested (128 DAP) and divided into two subsamples, including air-dried and field-moist soil samples. The air-dried soil samples were ground and sieved through a 2 mm sieve, while the field-moist soil samples were packed in plastic containers and immediately refrigerated at 4°C to minimize microbial activity.

2.4. Laboratory Analyses

2.4.1. Humic Acid and Flue Gas Desulfurization Gypsum Analyses

The pH and EC of both HA and FG were determined using a 1:5 soil amendment to DI water ratio [42]. Total N and TOC were performed using dry combustion with a CN analyzer (Multi N/C 2100s, Analytik Jena Germany). The CEC of HA was determined using 1 M ammonium acetate (NH₄OAc), pH 7 [43]. Total Ca and S concentrations in HA were analyzed using hot acid digestion (7 mL of HClO₄ at 190°C until the color of suspension was clear) [42] and those for FG was determined by aqua regia (3:1 HCl: HNO₃ at 130°C for 1 hour) [44]. The concentrations of Ca and S were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Analytic Jena PQ 9000).

2.4.2. Soil Analyses

Soil pH and redox potential (Eh) under field conditions were measured using a portable pH meter (Hanna Instruments, HI 98103) and an oxidation-reduction potential (ORP) meter (Hanna Instruments, HI 8424), respectively. Air-dried soil samples were determined for particle size distribution, total N, TOC, exchangeable Ca, and CEC. Particle size distribution of the initial soil was determined by the pipette method [45]. Total N and TOC were determined using dry combustion with a CN analyzer (Multi N/C 2100s, Analytik Jena Germany). Exchangeable Ca and CEC were analyzed using 1 M NH₄OAc at pH 7 [43]. The total concentrations of Ca and S were determined

using aqua regia digestion (1:3 HNO₃: HCl at 130°C for 1 h) [44] and their concentrations were determined using ICP-OES (Analytic Jena PQ 9000).

Field-moist soil samples were prepared for exchangeable S, NH₄-N (NH₄-N), and NO₃-N (NO₃-N) analysis. The exchangeable S concentration was extracted with Mehlich-3 solution and quantified by ICP-OES (Analytic Jena PQ 9000) [43]. NH₄-N and NO₃-N were extracted by 2 M KCl and 0.5 M K₂SO₄, respectively. NH₄-N concentration was determined using the salicylate-sodium hypochlorite, while NO₃-N was determined using the salicylic acid-sodium hydroxide [46]. The concentration of NH₄-N and NO₃-N were determined by colorimetric method using a spectrophotometer (SP-UV 300) at 650 and 410 nm, respectively [46].

2.4.3. Plant Analyses

The plant samples, including grain, straw, and root biomass, were digested using hot acid digestion with 7 ml of HClO₄ at 190°C until the color of suspension became clear [42]. The N concentration in the solution was determined using the Kjeldahl distillation method [46]. The total N uptake in rice was computed by multiplying the N concentration in grain, straw, and root by the oven-dried biomass.

NUE was determined by the difference in total N uptake, derived from grain, straw, and root biomass, between pots that received fertilizer and soil amendments and those that did not receive any fertilizers and soil amendments, as explained in equation (1) [28].

$$\text{NUE (\%)} = \frac{\text{Nf}-\text{Nu}}{\text{Total amount of N applied (kg ha}^{-1}\text{)}} \times 100 \quad (1)$$

where Nf is the amount (kg ha⁻¹) of total N uptake of rice in the pot with fertilizer and soil amendments. Nu is the amount (kg ha⁻¹) of total N uptake of rice in the pot without fertilizer and soil amendments.

NAE, the grain production per unit of fertilizer applied, was calculated by the ratio of the difference of grain yield of the fertilized pot and unfertilized pot to the total amount of N applied as shown in equation (2) [28].

$$\text{NAE (kg kg}^{-1}\text{)} = \frac{\text{Gf}-\text{Gu}}{\text{Total amount of N applied (kg ha}^{-1}\text{)}} \quad (2)$$

where Gf is the amount (kg ha⁻¹) of grain yield of the pot with fertilizer and soil amendments. Gu is the amount (kg ha⁻¹) of grain yield of the pot without fertilizer and soil amendments.

2.5. Statistical Analyses

All data were analyzed using a three-way analysis of variance (ANOVA) along with mean comparisons using least significant difference (LSD) ($P < 0.05$) to determine the effect of fertilizer, HA, FG, and their interactions on soil properties and rice yields. The data describing the relationship between yield components and agronomic attributes were analyzed using principal component analysis (PCA) and regression analysis at ($P < 0.05$). Data analyses were conducted using Statistica software version 8.0 while graphical visualizations were created using SigmaPlot version 11 and OriginPro 2018.

3. Results and Discussion

3.1. Effects of Fertilizer, Humic Acid, and Gypsum Applications on Soil Properties

The effects of fertilizer, HA, and FG applications on paddy soil properties are shown in Table 3 and Figures 1 and 2.

After harvest, the soil pH ranged from 6.6 to 7.2 and were not influenced by the applications of chemical fertilizer, HA, and FG (Table 3) (Figure 1a). However, the soil pH values increased by approximately 40% to 53%, compared to the initial soil pH (4.7) (Table 1). The soil pH alteration is due to the reduction of ferric iron (Fe³⁺) into ferrous iron (Fe²⁺) under waterlogged conditions, which consume protons and raise pH levels [47,48].

Soil Eh was also unaffected by chemical fertilizer, HA, and FG. The soil Eh ranged from -141 to -85 mV (Figure 1b). These values indicate that the studied soils are under reducing conditions, commonly observed under anaerobic conditions where soil microbes utilize alternative electron acceptors to compensate for the lack of oxygen [49].

TOC was neither affected by fertilizer nor FG. However, the TOC was affected by HA addition (Table 3). The TOC in soil treated with HA (2.3 g kg^{-1}) was higher compared to those without HA (2.2 g kg^{-1}). The integrated use of F1H1G1 achieved the highest TOC (2.4 g kg^{-1}) (Figure 1c), likely due to HA being rich in stable organic carbon which enhanced TOC in the soil (Table 1). Additionally, FG released Ca that plays an important role in TOC stabilization and accumulation as Ca being a polyvalent cation acts as a bridge between negative charge of clay particle and organic colloids during deprotonation of the carboxylic (COOH) and phenolic OH functional groups [50].

Table 3. Soil properties influenced by applications of fertilizer, humic acid, and flue gas desulfurization gypsum under rice cultivation in an acidic paddy soil.

Soil Properties	Soil pH	Eh	TOC	CEC	Total N	NH ₄ -N	NO ₃ -N	Exc. Ca	Exc. S
		(mV)	(g kg ⁻¹)	(cmol kg ⁻¹)	(g kg ⁻¹)	(-----mg kg ⁻¹ -----)			
Fertilizer (F)									
F1	6.8	-100	2.3	3.1a	1.5a	16b	5.2a	280	57
F2	6.9	-110	2.3	2.2b	1.4b	19a	4.4b	295	63
<i>P value</i>	0.448	0.217	0.168	<0.001	0.052	0.013	0.023	0.173	0.167
Humic acid (HA)									
H0	6.8	-97	2.2b	2.3b	1.4b	17	5.2a	286	60
H1	6.8	-113	2.3a	3.0a	1.6a	19	4.4b	290	60
<i>P value</i>	0.913	0.064	0.003	<0.001	<0.001	0.109	0.038	0.741	0.928
Gypsum (FG)									
G0	7.0	-104	2.3	2.7ab	1.4	18a	4.2b	284b	54b
G1	6.8	-111	2.3	2.8a	1.5	20a	4.6ab	250b	50b
G2	6.8	-101	2.2	2.4b	1.5	15b	5.7a	329a	77a
<i>P value</i>	0.122	0.514	0.136	0.023	0.404	0.001	0.012	<0.001	<0.001
Interactions (<i>P value</i>)									
F × HA	0.238	0.343	0.320	0.099	0.01	0.089	0.362	<0.001	0.751
F × FG	0.721	0.577	0.143	0.450	0.696	0.116	0.028	0.085	0.352
HA × FG	0.802	0.174	0.319	0.006	0.003	0.004	0.024	<0.001	0.158
F × HA × FG	0.313	0.697	0.379	<0.001	<0.001	0.267	0.681	0.018	0.682

HA = Humic acid; FG = Flue gas desulfurization gypsum; F1 = Fertilizer application rate based on farmer practices; F2 = Fertilizer application rate based on rice nutrient requirements; H0 = No HA; H1 = HA application at 975 kg ha^{-1} ; G0 = No FG; G1 = FG application rate based on gypsum requirement at 636 kg ha^{-1} ; G2 = FG application rate based on Ca required by rice at 23 kg ha^{-1} . Eh = Field redox potential; TOC = Total organic carbon; CEC = Cation exchange capacity; N = Total nitrogen; NH₄-N = Exchangeable ammonium nitrogen; NO₃-N = Exchangeable nitrate nitrogen; Exc. Ca = Exchangeable calcium; Exc. S = Exchangeable sulfur. Mean value followed by different letters showed significant differences at $P < 0.05$.

CEC was significantly improved by chemical fertilizer, HA, and FG applications. Soil treated with H1 and G1 had higher CEC values (3.0 and 2.8 cmol kg⁻¹, respectively) (Table 3). The interaction effect of F1H1 and H1G1 significantly elevated CEC to 3.3 and 3.4 cmol kg⁻¹, respectively (Figures 2a and 2b). The highest CEC was recorded under F2H1G1 (3.5 cmol kg⁻¹) (Figure 1d). CEC was positively related with TOC ($R^2 = 0.13$) ($P < 0.05$) (Figure 3a), indicating that the addition of HA can increase CEC in the soils by providing the negative charges, derived from its functional groups such as carboxylic and phenolic groups [11,22,51]. FG application helps increase CEC in soils because released Ca²⁺ displaces proton (H⁺) and Al³⁺ that are adsorbed onto soil surfaces, increasing the negative charges in soils [52]. In addition, Ca released from FG favors soil aggregate formation, which increase surface area for cation exchange, thereby indirectly benefiting CEC [28,30].

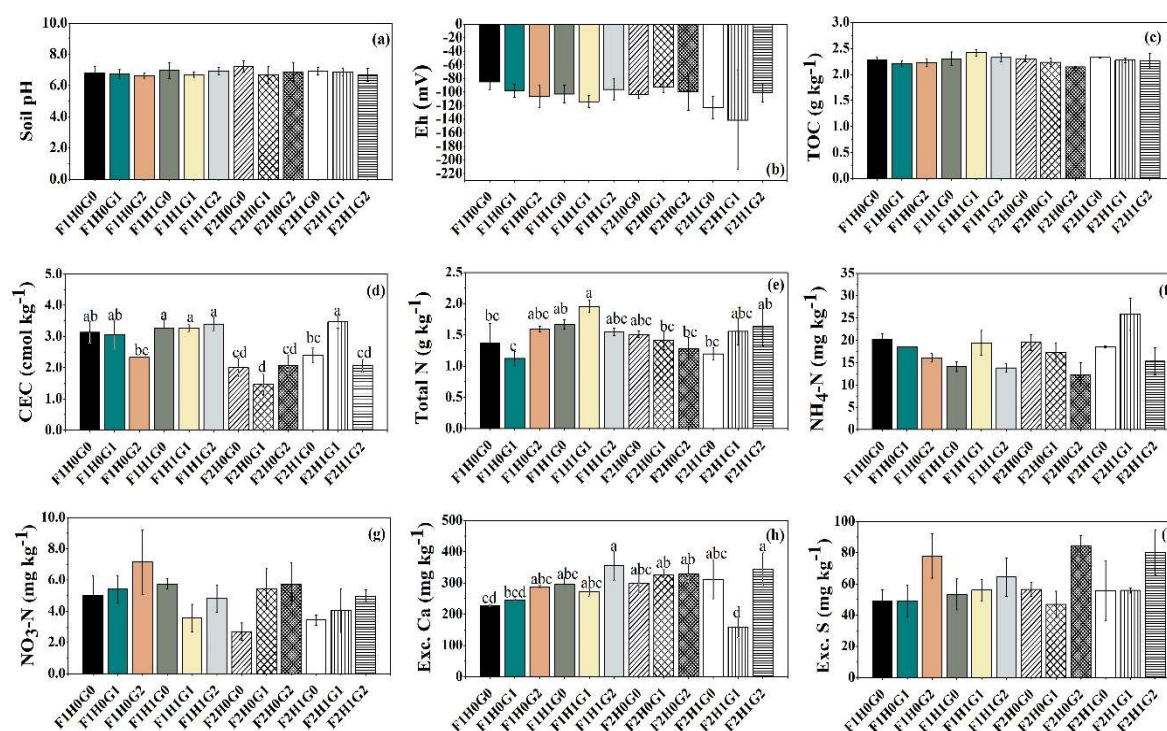


Figure 1. The interaction effect of fertilizer, humic acid (HA), and flue-gas desulfurization gypsum (FG) on soil properties after soil amendments incorporation. Soil pH (a); Eh (b); total organic carbon (TOC) (c); cation exchange capacity (CEC) (d); total nitrogen (Total N) (e); exchangeable ammonium nitrogen (NH₄-N) (f); exchangeable nitrate nitrogen (NO₃-N) (g); exchangeable calcium (Exc. Ca) (h); exchangeable sulfur (Exc. S) (i). F1 = Fertilizer application rate based on farmer practices; F2 = Fertilizer application rate based on rice nutrient requirements; H0 = No HA; H1 = HA application at 975 kg ha⁻¹; G0 = No FG; G1 = FG application rate followed gypsum requirement at 636 kg ha⁻¹; G2 = FG application rate based on Ca required by rice at 23 kg ha⁻¹. Mean value followed by different letters showed significant differences at $P < 0.05$.

Total N ranged from 1.1 to 2.0 g kg⁻¹ (Figure 1e), with significant increases observed under F1 (1.5 g kg⁻¹) and H1 (1.6 g kg⁻¹) (Table 3). The interaction effect of F1H1 and H1G1 significantly increased total N to 1.7 g kg⁻¹ and 1.8 g kg⁻¹, respectively (Figures 2c and 2d). The highest total N was achieved by integrated F1H1G1 practice (2.0 g kg⁻¹) (Figure 1e). The increase of total N in F1 and H1 was due to F1 supplying higher total N to the soil (Table 2) and HA containing high N content (Table 1), respectively. The highest total N in F1H1G1 was attributed to the fact that N was supplied by fertilizer, HA, and FG, with a total N input of 85.76 kg N ha⁻¹ to the soil (Table 2).

NH₄-N was significantly increased by the application of fertilizer, FG, and the combination of HA and FG (Table 3 and Figure 2e). F2 and H1 showed similar NH₄-N concentrations (19 mg kg⁻¹ for both), while the G1 increased NH₄-N to 20 mg kg⁻¹ (Table 3). The H1G1 significantly elevated NH₄-N

to 23 mg kg⁻¹ (Figure 2e). Moreover, NH₄-N was higher under F2H1G1 (26 mg kg⁻¹) than other treatments (Figure 1f).

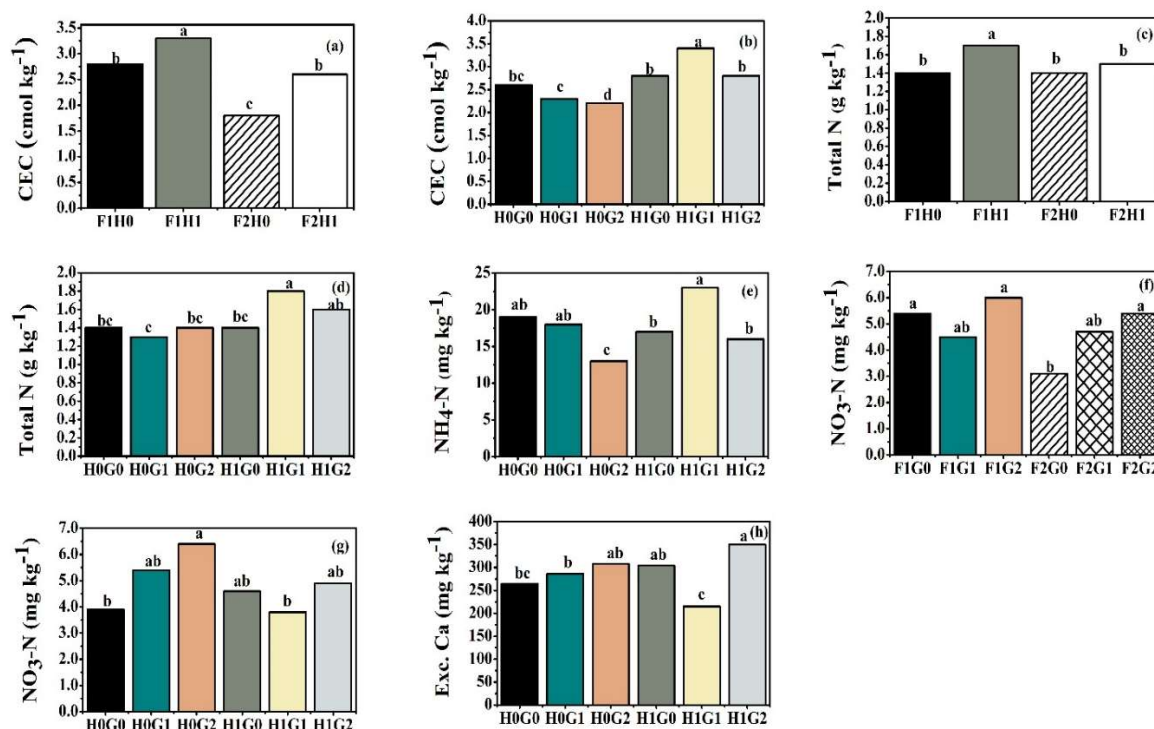


Figure 2. Two factor interaction effects of fertilizer, humic acid (HA), and flue-gas desulfurization gypsum (FG) on soil properties after soil amendments incorporation. Cation exchange capacity (CEC) (a and b); total nitrogen (N) (c and d); exchangeable ammonium nitrogen (NH₄-N) (e); exchangeable nitrate nitrogen (NO₃-N) (f and g); and exchangeable calcium (Exc. Ca) (h). F1 = Fertilizer application rate based on farmer practices; F2 = Fertilizer application rate based on rice nutrient requirements; H0 = No HA; H1 = HA application at 975 kg ha⁻¹; G0 = No FG; G1 = FG application rate followed gypsum requirement at 636 kg ha⁻¹; G2 = FG application rate based on Ca required by rice at 23 kg ha⁻¹. Mean value followed by different letters showed significant differences at $P < 0.05$.

NO₃-N was significantly affected by fertilizer, HA, FG, fertilizer × FG, and HA × FG (Table 3). The NO₃-N concentrations were notably increased either by F1 (5.2 mg kg⁻¹) or G2 (5.7 mg kg⁻¹) (Table 3). The F1G2 slightly increases NO₃-N to 6.0 mg kg⁻¹ (Figure 2f). Both sole H1 (4.4 mg kg⁻¹) and G1 (4.6 mg kg⁻¹) treatments and their interactions of H1G1 significantly reduced NO₃-N to 3.8 mg kg⁻¹ (Table 3) (Figure 2g), which were lower than in the initial soil (12 mg kg⁻¹) (Table 1). The highest NO₃-N was in F1H0G2 (7.2 mg kg⁻¹) (Figure 1g). The bivariate relationship revealed that NH₄-N had a negative relationship with NO₃-N ($R^2 = 0.11$) ($P < 0.05$) (Figure 3b). This study was consistent with the study by Chen et al. [36] who reported that when HA was applied together with FG, NH₄-N retention on soil colloidal surfaces is not nitrified and improved. The S derived from FG hindered NH₄-N transformation to NO₃-N by forming complexes with NH₄⁺ to form ammonium sulfate ((NH₄)₂SO₄) [53]. Additionally, the HA can adsorb NH₄-N due to its negative charge, which slows the transformation of NH₄-N to NO₃-N through nitrification, leading to a decrease in nitrogen losses through leaching, volatilization, and denitrification [23].

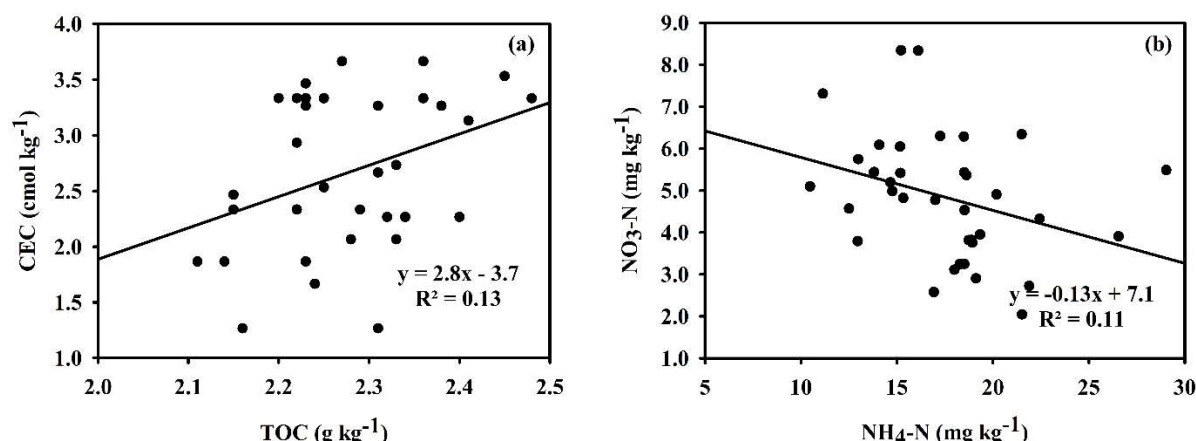


Figure 3. Bivariate relationship ($n = 36$) between total organic carbon (TOC) and cation exchange capacity (CEC) (a) and exchangeable ammonium nitrogen ($\text{NH}_4\text{-N}$) and exchangeable nitrate nitrogen ($\text{NO}_3\text{-N}$) (b). Significant differences at $P < 0.05$.

The application of G2 increased the concentrations of exchangeable Ca to 329 mg kg^{-1} , which was 1.3-fold higher than that in G1 (250 mg kg^{-1}) (Table 3). The H1G2 significantly enhanced exchangeable Ca to 350 mg kg^{-1} (Figure 2h). Exchangeable Ca concentrations after applying FG, especially G2, increased by 1.6 to 2.5 times (Table 3) higher than initial soil (95 mg kg^{-1}) (Table 1). The higher amount of exchangeable Ca was achieved by F1H1G2 (355 mg kg^{-1}), which is not significantly different from F2H1G2 (345 mg kg^{-1}) (Figure 1h). The low concentration of exchangeable Ca in G1 treatment is attributed to excessive Ca supply triggered a chemical reaction in the soil, i.e., exchangeable Ca reacts with P to form calcium phosphate minerals such as brushite ($\text{Ca}(\text{PO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$), which is not available to plant [54,55]. Thus, this study suggested that a suitable FG application rate in paddy field conditions should be considered based on Ca required by rice.

Exchangeable S ranged from 47 to 84 mg kg^{-1} (Figure 1i). Exchangeable S was recorded higher under G2-treated soil (77 mg kg^{-1}) compared to G1-treated soil (50 mg kg^{-1}) (Table 3). The soil treated with FG elevated exchangeable S due to FG supplying S to the soil as FG contained high amounts of S (Table 1). The lower concentration of exchangeable S in G1 compared to that of G2 is due to the lower Eh value in G1 (-111 mV) (Table 3). A higher FG application rate supplied more sulfate ions (SO_4^{2-}) to the soil and served as electron acceptor, producing hydrogen sulfide (H_2S) that led to lower Eh. A higher reduction state transforms SO_4^{2-} to H_2S which is prone to volatilization. Eventually, the exchangeable S depleted [56].

3.2. Yield, Nitrogen Uptake, Nitrogen Use Efficiency, and Nitrogen Agronomic Efficiency of Rice

Straw biomass was neither affected by fertilizer, HA, FG, nor their interactions (Table 4). Straw biomass ranged between 14 and 16 t ha^{-1} (Figure 4a). The highest straw biomass (16 t ha^{-1}) was under F1H0G0, F1H1G0, and F1H1G2. Whereas the lowest straw biomass was under F1H0G1 and F2H0G1 (14 t ha^{-1}) (Figure 4a).

Root biomass was higher in F1 (9.5 t ha^{-1}) and H0 (9.3 t ha^{-1}) than their corresponding counterparts of different rates (Table 4). Meanwhile, G2 had the highest root biomass of 10 t ha^{-1} , compared to those treated with G1 (8.3 t ha^{-1}) and G0 (8.5 t ha^{-1}) (Table 4). The interaction of fertilizer \times HA and HA \times FG significantly affected root biomass (Table 4). The F1H0 and H0G2 significantly increased root biomass to 11 t ha^{-1} (Figures 5a and 5b), while F1H0G2 showed the highest root biomass (13 t ha^{-1}) (Figure 4b).

Table 4. Yield, total N uptake, and nitrogen use efficiency as influenced by applications of fertilizer, humic acid, and flue gas desulfurization gypsum under rice cultivation in the acidic paddy soil.

Treatment	Straw biomass	Root biomass	Grain yield	Total N uptake	NUE	NAE
	(-----t ha ⁻¹ -----)			(kg ha ⁻¹)	(%)	(kg kg ⁻¹)
Fertilizer (F)						
F1	15	9.5a	7.3	68	31b	28
F2	15	8.1b	7.1	67	36a	30
P value	0.099	<0.001	0.230	0.657	0.008	0.234
Humic acid (HA)						
H0	15	9.3a	7.0b	65b	30b	25b
H1	15	8.3b	7.4a	70a	36a	33a
P value	0.730	0.014	0.004	0.013	0.004	<0.001
Gypsum (FG)						
G0	15	8.5b	7.3	69	36	31a
G1	14	8.3b	6.9	66	31	26b
G2	15	10a	7.3	68	33	30a
P value	0.120	0.011	0.094	0.429	0.101	0.034
Interactions (P value)						
F x HA	0.499	0.008	0.903	0.177	0.161	0.073
F x FG	0.243	0.257	0.368	0.334	0.853	0.631
HA x FG	0.662	0.027	0.768	0.053	<0.001	0.001
F x HA x FG	0.709	0.218	0.184	0.073	<0.001	0.012

HA = Humic acid; FG = Flue gas desulfurization gypsum; F1 = Fertilizer application rate based on farmer practices; F2 = Fertilizer application rate based on rice nutrient requirements; H0 = No HA; H1 = HA application at 975 kg ha⁻¹; G0 = No FG; G1 = FG application rate based on gypsum requirement at 636 kg ha⁻¹; G2 = FG application rate based on Ca required by rice at 23 kg ha⁻¹. Total N uptake = Total nitrogen uptake; NUE = Nitrogen use efficiency; NAE = Nitrogen agronomic efficiency. Mean value followed by different letters showed significant differences at *P* < 0.05.

For grain yield, although fertilizer application showed a nonsignificant effect on grain yield, F2 can reduce the amounts of N input by 14.5% without a significant decline in grain yield, compared to F1. Grain yield significantly increased by H1 addition (7.4 t ha⁻¹) (Table 4). Although rice grain yield was not responsive to the interaction of fertilizer, HA, and FG, this study found that both F1H1G0 and F1H1G2 achieved the maximum grain yield (7.7 t ha⁻¹), whereas both F1H0G1 (6.8 t ha⁻¹) and F2H0G1 (6.6 t ha⁻¹) gained the minimum grain yield (Figure 4c). Therefore, this study highlighted the fact that the application of FG at a high rate based on gypsum requirement at 636 kg ha⁻¹ (G1) restricts straw biomass and grain yield in the studied soil acidic paddy soil.

Total N uptake ranged from 57 to 74 kg ha⁻¹ (Figure 4d) and was significantly increased by H1 (70 kg ha⁻¹) (Table 4). NUE was significantly influenced by both fertilizer application rates and HA. F2 and H1 increased NUE to 36% (Table 4), while the F1H1G2 resulted in the highest NUE (39%) under farmer practices (Figure 4e). Under rice nutrient requirement-based fertilization, F2H1G1 maximizes the NUE to 46 % (Figure 4e). NAE was significantly improved by H1 and further enhanced by multiple interactions (fertilizer x HA, fertilizer x HA x FG, and HA x FG) (Table 4). Applying F2 (30 kg kg⁻¹) tended to give higher NAE values than F1 (28 kg kg⁻¹) and were significantly increased by H1 addition (33 kg kg⁻¹) (Table 4). Both the F1H1G0 and F1H1G2 produced an optimal NAE (32 kg ha⁻¹) under farmer practices, whereas the F2H1G1 practice maximized the NAE to 41 kg ha⁻¹ for rice grown under rice nutrient requirement-based fertilization (Figure 4f).

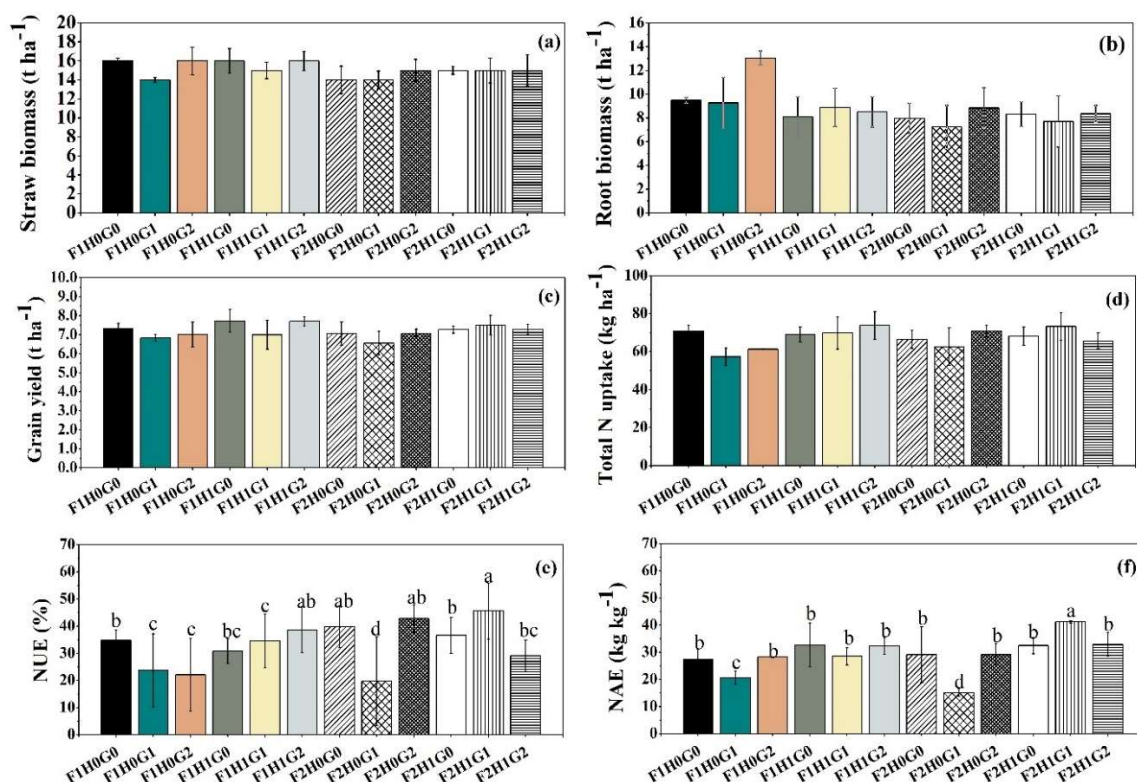


Figure 4. The interaction effect of fertilizer, humic acid (HA), and flue-gas desulfurization gypsum (FG) on straw biomass (a); root biomass (b); grain yield (c); total nitrogen (N) uptake (d); nitrogen use efficiency (NUE) (e); nitrogen agronomic efficiency (NAE) (f). F1 = Fertilizer application rate based on farmer practices; F2 = Fertilizer application rate based on rice nutrient requirements; H0 = No HA; H1 = HA application at 975 kg ha⁻¹; G0 = No FG; G1 = FG application rate followed gypsum requirement at 636 kg ha⁻¹; G2 = FG application rate based on Ca required by rice at 23 kg ha⁻¹. Mean value followed by different letters showed significant differences at $P < 0.05$.

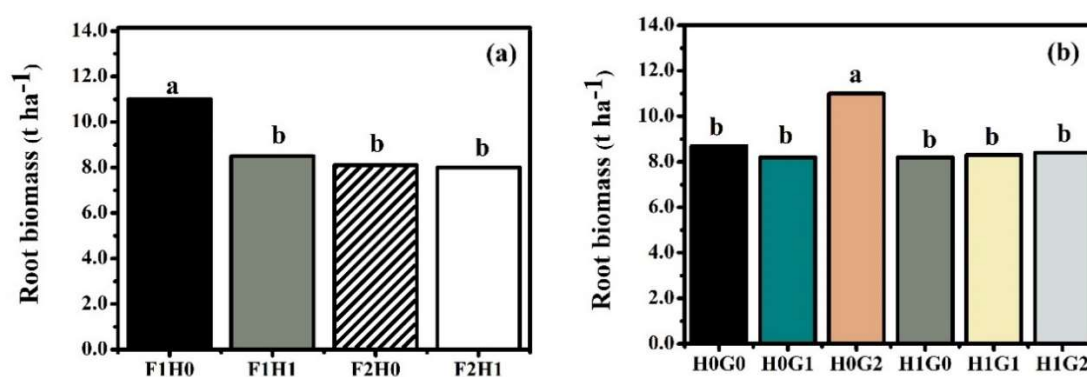


Figure 5. Two factor interaction effect of fertilizer, humic acid (HA), and flue-gas desulfurization gypsum (FG) on root biomass (a and b). H0 = No HA; H1 = HA application at 975 kg ha⁻¹; G0 = No FG; G1 = FG application rate followed gypsum requirement (636 kg ha⁻¹); G2 = FG application rate based on Ca required by rice (23 kg ha⁻¹). Mean value followed by different letters showed significant differences at $P < 0.05$.

The application of fertilizer according to rice nutrient requirements reduces the use of chemical fertilizers without adversely affecting rice yield. F2 provided appropriate nutrients supply to achieve optimum rice yield. This study, therefore, advocates nutrient applications based on crop nutrient requirement, such as rice, for its crucial role in achieving precision nutrient management and sustainability. HA application contributed to higher grain yield, NUE, and NAE, primarily by

stimulating the nutrient uptake (Table 4) as the HA incorporation increases the accumulation of soil nutrient availability like $\text{NH}_4\text{-N}$ (Table 3). The F2H1G1 practice did not achieve the higher rice yield like F1H1G0 and F1H1G2 did, but this practice achieves maximum NUE and NAE. This finding indicates that higher NUE and NAE under F2H1G1 practice is mainly attributed to lower total nutrient input (71.76 kg ha^{-1}) to the soil. i.e., 19% lower than F1H1G0 (85.68 kg ha^{-1}) and F1H1G2 practice ($85.683 \text{ kg ha}^{-1}$) (Table 2). Conversely, the F1H1G1, F1H0G1, and F2H0G1 practices where the FG was applied at a higher rate (636 kg ha^{-1}) tended to reduce rice yield. Previous studies reported the crop response to FG application at different rates to slightly acidic soil (pH 6.3-6.5) and revealed that FG applied at a higher rate led to yield reduction because Ca, released from FG, induced nutrient imbalance and lower nutrients P, K and Mg uptake [28,57]. According to this current study, the decline in rice yield is owing to G1 releasing a large amount of Ca to the soil, which potentially inhibited N uptake as found by previous work that Ca released from FG plays a crucial role in regulating N absorption [31,58]. Therefore, this finding suggests that careful consideration should be made when considering an FG application. Additionally, the FG should be applied based on Ca needed by rice (23 kg ha^{-1}) as it increased soil exchangeable Ca and S. This finding can be applied to other types of gypsum to be applied a paddy soils.

3.3. Relationship Between Rice Yield, Nitrogen Uptake, Nitrogen Use Efficiency, and Nitrogen Agronomic Efficiency

Principal component analysis (PCA), performed using the basis of the standardized average values of soil properties (including soil pH, Eh, TOC, CEC, total N, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, exchangeable Ca, and exchangeable S), rice grain, straw biomass, root biomass, total N uptake, NUE, and NAE, is presented in Figure 6.

PCA showed that Eh, exchangeable Ca, exchangeable S, $\text{NO}_3\text{-N}$, and root biomass were mainly associated with F1H0G2, F2H0G2, and F2H1G2 (Figure 6). This is attributed to FG-enhanced root development due to supplying exchangeable S (Table 3) [59]. Higher concentrations of exchangeable S in the soil treated by G2 were discussed in section 3.1.

Furthermore, total N, CEC, straw biomass, grain yield, total N uptake, NUE, and NAE were associated with F1H1G0 and F1H1G2 (Figure 6). The bivariate relationship was positive between rice grain yield and straw biomass ($R^2 = 0.48$) ($P < 0.05$) (Figure 7a). In addition, grain yield was positively associated with total N uptake ($R^2 = 0.38$) ($P < 0.05$) (Figures 7b), indicating that increased straw biomass contributes to increase grain production because higher straw biomass supports higher photosynthesis rate and nutrients reserves which are essential for grain development [60]. Furthermore, this study suggested that total N uptake is critical for rice grain yield since N is a fundamental component of chlorophyll, which facilitates photosynthesis and carbohydrate synthesis for grain filling [61].

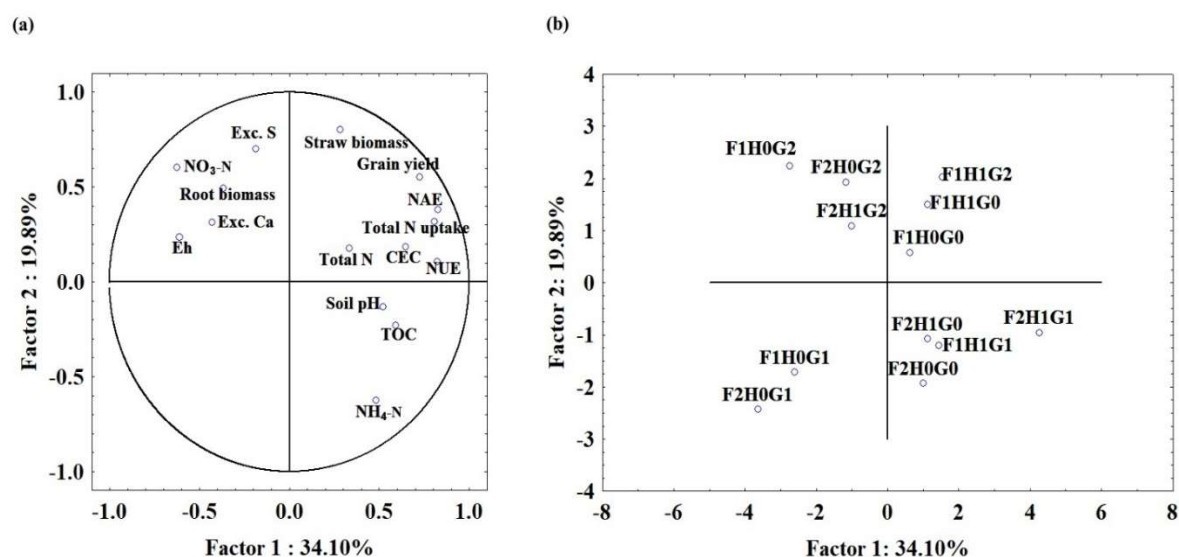


Figure 6. Principal component analysis based on standardized average data for rice grain, straw biomass, root biomass, total nitrogen (N) uptake, N use efficiency (NUE), and N agronomic efficiency (NAE), and soil properties of an acidic paddy soil. (a) distribution of properties (variables) and (b) distribution of soils treated by different application rate of fertilizer, humic acid (HA), flue gas desulfurization gypsum (FG) (cases) for all treatments. F1 = Fertilizer application rate based on farmer practices; F2 = Fertilizer application rate based on rice nutrient requirements; H0 = No HA; H1 = HA application at 975 kg ha⁻¹; G0 = No FG; G1 = FG application rate followed gypsum requirement at 636 kg ha⁻¹; G2 = FG application rate based on Ca required by rice at 23 kg ha⁻¹.

Straw biomass was positively associated with both total N uptake ($R^2 = 0.21$) ($P < 0.05$) and root biomass ($R^2 = 0.13$) ($P < 0.05$) (Figures 7c and 7d), indicating that total N uptake contributes more to increasing straw biomass as N is required for cell division and growth [62,63]. Improving underground biomass contributes to higher straw biomass as an extensive root system absorbs more nutrients and water that can be transported to the aboveground biomass [64].

NUE was positively correlated with total N uptake and grain yield ($R^2 = 0.38$ and 0.13 , respectively) ($P < 0.05$) (Figures 7e and 7f). These findings underscore the importance of enhancing total N uptake in improving NUE as total N uptake is a key component for NUE computation [65]. Moreover, grain yield, total N uptake, and straw biomass were associated with NAE ($R^2 = 0.48$, 0.20 and 0.18 , respectively) ($P < 0.05$) (Figures 7g-7i). The NAE is defined as the grain yield produced per unit of N applied [65]. Therefore, this study indicates that improving grain yield leads to achieving higher NAE, which is a crucial component of the ISFM [66]. The study by Vanlauwe et al. [66] revealed that higher NAE can enhance economic returns for farmers. This current study, therefore, proposes that the ISFM of fertilizer application based on farmer practices combined with HA (F1H1G0) or with HA and FG based on rice requirement (F1H1G2) are optimal soil management practice for adopting in an acidic paddy soil because these practices potentially sustain rice production and NAE.

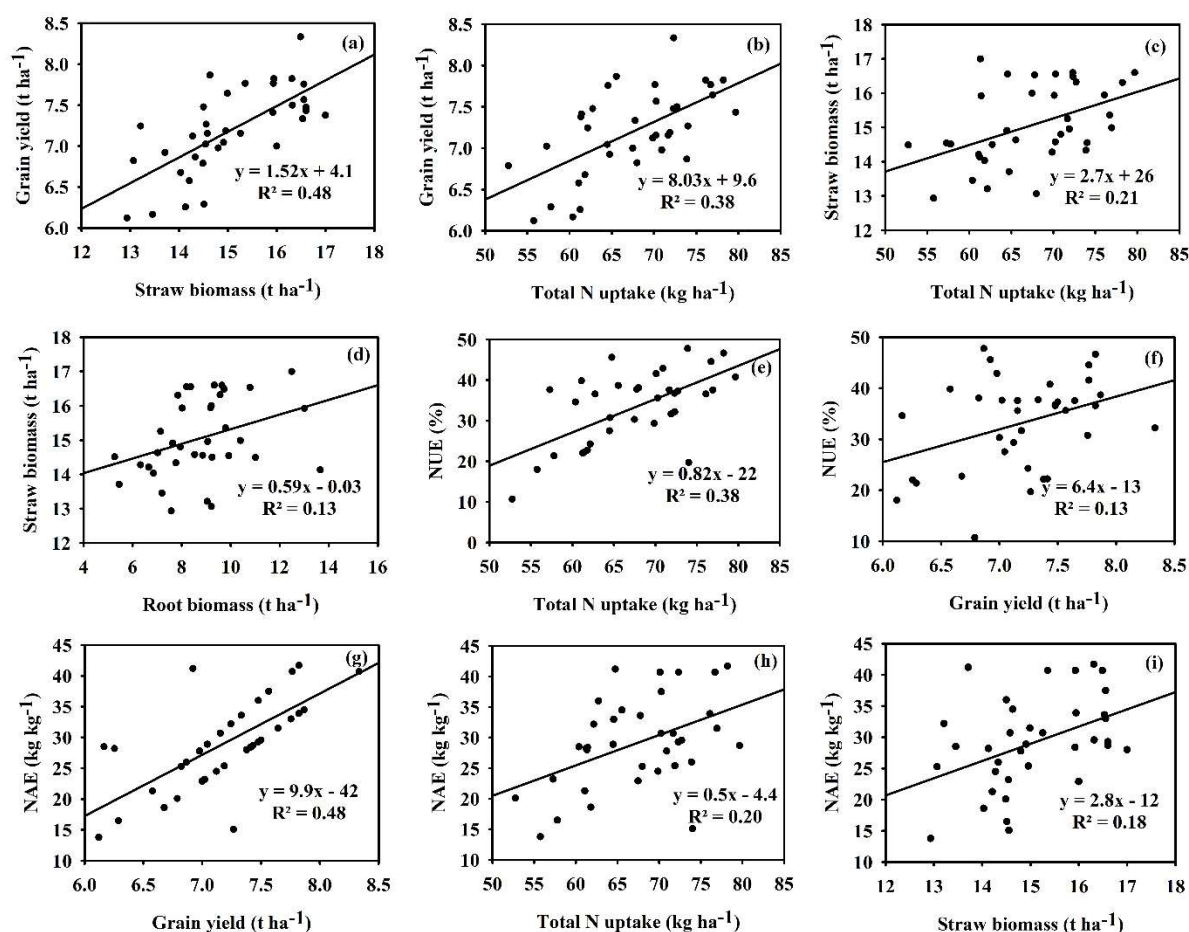


Figure 7. Bivariate relationship ($n = 36$) between grain yield and straw biomass (a) and total N uptake (b); straw biomass and total nitrogen (N) uptake (c) and root biomass (d); nitrogen use efficiency (NUE) and total N uptake (e) and grain yield (f); nitrogen agronomic efficiency (NAE) and grain yield (g), total N uptake (h) and straw biomass (i). Significant differences at $P < 0.05$.

The increase in rice yield in soil treated with HA is due to HA increasing the CEC, TOC, and NH_4 -N, all of which in turn promote nutrient uptake and rice productivity. This is consistent with previous studies showing that HA applications (e.g., $1500\ kg\ ha^{-1}$ and $20\ mg\ CL^{-1}$) promoted crops growth and yield (e.g., rice and maize) in black soil in a typical cold region and hydroponic system, respectively [67,68]. Furthermore, the positive interactive effect of HA and FG in the F1H1G2 results in higher grain yield, straw biomass, and NAE, compared to the other treatments. Therefore, this study proposes that the integration of fertilizer application based on farmer practice, either with HA alone or combined with FG based on rice need at $23\ kg\ ha^{-1}$ is proposed as an effective strategy for improving grain yield and NAE in acidic paddy soil.

Other ISFM strategies, such as F1H1G1, F2H0G0, F2H1G0, and F2H1G1, were associated with soil pH, TOC, and NH_4 -N. Additionally, the F2H1G1 was associated with NUE, total N uptake, and NAE, which was situated along the factor 1 axis (Figure 6). Higher TOC in the combined application of HA and FG ($636\ kg\ ha^{-1}$) was attributed to TOC supplied by HA (Table 1) and Ca derived from FG, forming complexes with OC to stabilize and accumulate TOC in the soil because their complexation can protect OC from microbial decomposition [28,50,69]. This showed that coapplication of HA and FG applied following gypsum requirement ($636\ kg\ ha^{-1}$) under both fertilizer regimes of soils fertilized pertaining to farmer practice and rice requirements can improve properties of the studied acidic paddy soil but they did not bring about additional benefits to crop performance, i.e., NUE, and NAE. However, this study highlights that farmers should apply FG according to gypsum

requirements, along with fertilizer application rates based on rice's needs, to enhance total N uptake, NUE, and NAE.

4. Conclusions

This study determines the effects of integrated soil fertility management (ISFM) involving the coapplication of chemical fertilizer, humic acid (HA), and flue gas desulfurization gypsum (FG) on soil properties, rice yield, nitrogen (N) use efficiency (NUE), and N agronomic efficiency (NAE) in a tropical acidic paddy soil. Fertilizer primarily enhances total N and exchangeable $\text{NO}_3\text{-N}$ ($\text{NO}_3\text{-N}$). HA incorporation improves soil TOC, CEC, total N, and exchangeable $\text{NH}_4\text{-N}$ ($\text{NH}_4\text{-N}$). FG incorporation improves exchangeable Ca, but requires careful management when it is applied alone. Coapplication of HA and FG based on gypsum requirement (636 kg ha^{-1}) in the acidic paddy soils improves total N, TOC, and $\text{NH}_4\text{-N}$. However, integrating FG at this rate with application of chemical fertilizer based on farmer practices adversely affect rice yield and total N uptake. On the other hand, applying FG at 23 kg ha^{-1} , whether alone or with HA improves exchangeable Ca and S under farmer practices. The optimal ISFM strategy combining the application of HA (975 kg ha^{-1}) and FG (23 kg ha^{-1}) significantly enhances soil properties and rice agronomic performance. The findings of this study highlight the optimum application rate of FG, which should be at 23 kg ha^{-1} , particularly in combination with HA, to maximize NUE, NAE, and rice yield. The higher FG application rates based on gypsum requirements should be avoided when paddy soils are fertilized using farmer practice, owing to the negative impacts on yield, total N uptake, and NUE. However, to improve total N uptake, NUE, and NAE, FG addition based on gypsum requirement should be applied with a fertilizer rate based on rice requirement.

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