

Ammoniacal and Nitrate nitrogen release pattern from biochar and biochar blended urea fertilizers in sandy soil

ABSTRACT

Biochar, an organic product of thermal decomposition of biomass in an oxygen limited environment can be used as a nutrient carrier to delay the release of nutrients into the soil, reduce nutrient leaching, and improve the nutrient utilization efficiency of fertilizers. Nutritional enhancement of biochar through fertilizer blending could be a low cost but high efficiency solution compared to non-blended fertilizers. However, the rate of nutrient release from the blended biochar fertilizer in different soils is ambiguous. Hence a 12 month incubation study was conducted in sandy soil (ultisol) of Thiruvananthapuram district of Kerala to elucidate the ammoniacal and nitrate nitrogen release rate and pattern from the produced paddy husk biochar, biochar and biochar bentonite (1:1) each blended with urea fertilizer in different ratios (1:0.5, 1:1, 1:2) including an absolute control. The individual effects of biochar, biochar-bentonite and urea were also studied. Paddy husk biochar was produced by the process of slow pyrolysis and biochar- blended urea fertilizers by the adsorbent process. To evaluate the influence of bentonite clay on the nutrient release pattern of biochar, it was blended with biochar and urea fertilizer. The highest total nitrogen content among the produced fertilizers was recorded in biochar: urea in 1:2 (33.04%) followed by biochar-bentonite: urea in a 1:2 ratio (31.13%). The incubation study revealed that the maximum release of ammoniacal nitrogen from soil+ urea fertilizer was at 30 days (115.73 mg kg⁻¹) followed by a sharp decline, maintaining a low value till the end of incubation, whereas the release was sustained and gradually increased to reach a maximum at the 180th day (117.6 mg kg⁻¹) for soil+ biochar: urea in 1:1 ratio. Nitrate nitrogen also followed the same trend with the maximum release observed for biochar: urea in 1:1 on the 150th day (151.2 mg kg⁻¹). The release of nitrate nitrogen was more than that of ammoniacal nitrogen throughout the incubation period for all the treatments. Among the blended fertilizers, content of both ammoniacal and nitrate nitrogen were comparatively less for biochar –bentonite blended urea fertilizers. Thus, blending of urea with biochar/ biochar-bentonite prolonged the duration of maximum nutrient release.

Keywords: Biochar, Biochar blended urea fertilizers, Ammoniacal and nitrate nitrogen

INTRODUCTION

Biochar is a stable carbon compound obtained by the thermal decomposition of organic materials under little or no oxygen and at relatively low temperatures (<700 °C), by the process of pyrolysis [1] and is recognized for its potential role in carbon sequestration, reducing greenhouse gas emissions, waste management, renewable energy production, soil health improvement, crop productivity enhancement and adsorption of pollutants [2]

Climate change mitigation through a reduction in net GHG (greenhouse gas) emissions by the process of carbon sequestration is possible through the application of biochar. Conversion of biomass C into biochar can sequester about 50% of the initial C

compared to the low amounts retained after biomass burning (3%) and biological decomposition (<10–20% after 5–10 years), thus yielding more stable soil C. During the pyrolysis process of biochar production, lignin, cellulose and hemicellulose in plant residue are converted to allotropes of carbon especially graphite crystals consisting of hexagonal carbon rings attached with some leftover hydrogen and oxygen, along with some minerals which constitute the skeletal structure of biochar which is very stable and hardly biodegradable, thus the carbon gets protected in skeletal structure [3]. Biochar is highly porous with an amazingly high surface area enabling it to retain more water, in addition to adsorption and retention of large amounts of nutrients by both physical and chemical processes and also improve soil biological properties.

The potential of biochar in nutrient sorption and carbon sequestration is not a new concept. Lehmann [4] compared soil fertility and leaching losses of nutrients between Fimic Anthrosol (a relict soil from pre-Columbian settlements with high organic C containing large proportions of black carbon) and a Xanthic Ferralsol from Central Amazon and reported that charcoal addition significantly delayed nutrient leaching losses and consequently enhanced plant growth and nutrition suggesting that biochar could improve soil health by improving nutrient retention and also serve as a nutrient source [5]. This suggests the probability of developing biochar blended fertilizers to improve nutrient retention and release.

The nutrients in chemical fertilizers can be efficiently loaded into biochar through the intimate contact between them [6]. The use efficiency of nitrogenous fertilizers is only approximately 33%, and hence an improvement in the efficiency of nitrogen use is of great environmental significance. The blending of nitrogenous fertilizers with eco-friendly biochar is a promising solution for this dilemma. The urea- blended biochar has a significantly higher apparent nitrogen utilization efficiency [7] and a relatively slow release pattern of nitrogen [8]. Thus biochar blended fertilizers significantly enhance the nutrient use efficiency and potentially shift the paradigm of mineral fertilization for green agriculture. In this study, the effect of biochar with blended urea fertilizer in different ratios on the rate and pattern of release of ammoniacal and nitrate nitrogen and the role of bentonite clay as a binding agent for the biochar blended fertilizers was investigated through a laboratory incubation study.

MATERIALS AND METHODS

Production of biochar and biochar blended fertilizers

Biochar was produced by the method of slow pyrolysis from paddy husk. The temperature build-up during pyrolysis of paddy husk was monitored using the digital infrared thermometer and was maintained between 300 and 350°C throughout the process. The process of slow pyrolysis continued up to 1.5 to 2 hr to produce the final product biochar [9]. The recovery percentage of biochar from paddy husk was nearly 50 per cent.

Biochar prepared from paddy husk was blended with urea through the adsorbent process to produce biochar blended nitrogen fertilizers in three ratios *viz.* biochar: urea in 1:0.5, 1: 1, and 1:2, by adding urea to biochar in the prescribed ratios, stirring for 30 minutes and allowing to cure for 24 h followed by shade drying [7]. Biochar-bentonite blended fertilizers were also produced by blending urea in the prescribed ratios with a mixture of biochar and bentonite in a ratio of 1:1. Thus six biochar- urea fertilizer blend combinations were produced *viz.* Biochar- Urea 1:0.5 (B:U= 1:0.5), Biochar- Urea 1:1 (B:U= 1:1), Biochar- Urea 1:2 (B:U= 1:2), Biochar- Bentonite: Urea 1:0.5 (Bio-Ben: U= 1:0.5), Biochar- Bentonite: Urea 1:1 (Bio-Ben: U= 1:1) and Biochar- Bentonite: Urea 1:2 (Bio-Ben: U= 1:2). The powdered and 2 mm sieved samples were digested and subjected to micro kjeldahl distillation to determine the nitrogen content of biochar and biochar blended fertilizers.

Ammoniacal and nitrate nitrogen release

Release of mineralizable nitrogen from the biochar and biochar- blended fertilizers was determined through a laboratory incubation study conducted at the Department of Soil Science, College of Agriculture, Vellayani, and Thiruvananthapuram, Kerala, India using a sandy soil. The soil was acidic in reaction (pH 4.5), low in soil electrical conductivity (0.05), low in available nitrogen (173.64 kg ha⁻¹), high in available phosphors (31.24 kg ha⁻¹) and low in available potassium (41.07 kg ha⁻¹). The experiment was conducted with ten treatments *i.e.* absolute control -5 kg soil alone (T₁), soil 5 kg + biochar (Paddy husk) @ 20 t ha⁻¹ (T₂), soil 5 kg + biochar- bentonite @ 20 t ha⁻¹ (T₃), soil 5 kg + biochar- urea - 1:0.5, 1:1, 1:2 (T₄-T₆), soil 5 kg+ biochar- bentonite: urea - 1:0.5, 1:1, 1:2 (T₇-T₉), soil 5 kg + urea (T₁₀). The surface soils (0-15 cm) for the incubation study was collected from the farmers field, Murukkumpuzha Thiruvananthapuram, Kerala located at 8.48⁰ north latitude and 76.92⁰ east longitudes at an altitude of 4m above MSL. Samples were mixed thoroughly and sieved through 2 mm sieve and the air dried and sieved soils (5 kg each) was placed in plastic containers and the treatments as per treatment details were imposed and mixed thoroughly. Blended fertilizers after characterization of nutrient content were added so as to supply nitrogen at the rate of 75 kg ha⁻¹. The soil samples after addition of treatments were arranged in a completely randomized design in triplicate and were incubated separately for one year (360 days). Distilled water was used to maintain the soil at field capacity during the entire period of incubation. Periodic sampling and analysis of the samples were conducted at 0, 15, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 days of incubation. The ammoniacal and nitrate nitrogen were analysed using steam distillation method [10]. Analysis of variance was used to test for treatment effects and treatment significance was tested using F test in ANOVA using GRAPES- General Rshiny Based Analysis Platform, Empowered by Statistics software. The level of significance was set at 0.05.

RESULTS AND DISCUSSIONS

Nitrogen content in biochar and blended fertilizers

The nitrogen contents of biochar and biochar blended with urea fertilizer through the adsorbent process are presented in Fig 1. Biochar blended with urea in 1:2 ratio had the

highest nitrogen content (33.04%) followed by biochar-bentonite: urea in 1:2 (31.13%) and biochar: urea in 1:1 (25.81). Biochar-Bentonite (1:1) mixed with urea in three ratios had lower nitrogen content than the respective biochar blended urea fertilizers. Puga [11] reported that nitrogen content of biochar -urea coated with bentonite was 20.9 % and that of biochar-urea with gum arabic and glycerol instead of bentonite was 38.3%. Zhang [7] also indicated that nitrogen adsorption was more efficient when biochar was blended with urea through the adsorbent process and the nitrogen content of biochar blended fertilizers solely depends on the amount of urea adsorbed to the biochar.

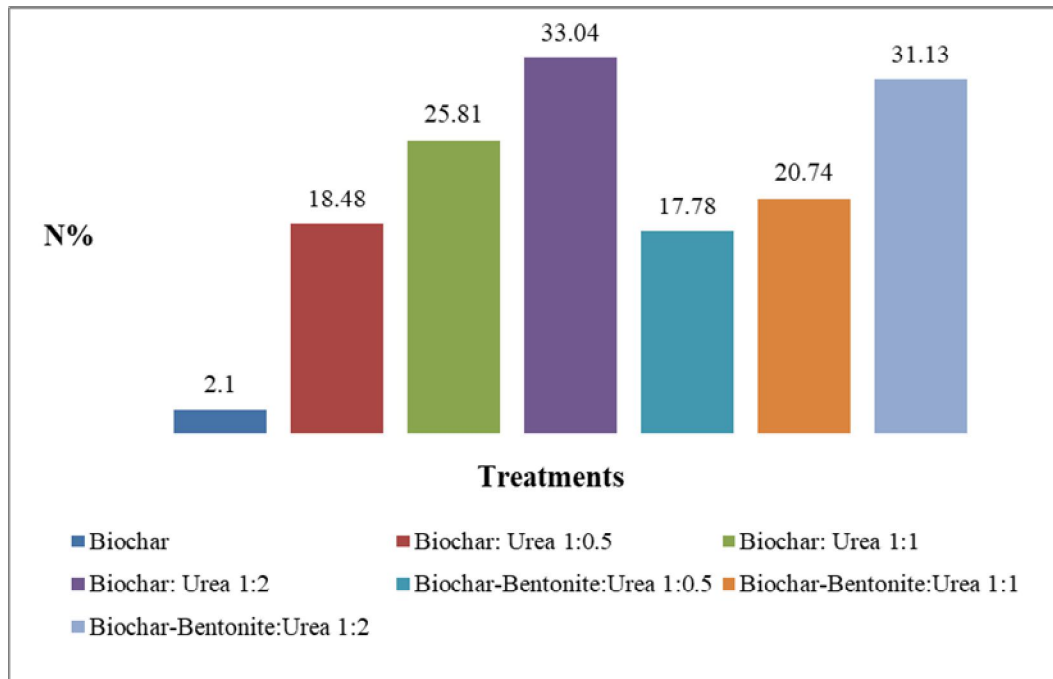


Fig 1: Nitrogen content in biochar and biochar blended urea fertilizers

Release pattern of ammoniacal nitrogen

Release pattern of ammoniacal nitrogen in sandy soil upon the addition of biochar and biochar blended urea fertilizers during the incubation study is depicted in Table 1. The NH_4^+ -N content was higher in soils treated with biochar and biochar blended fertilizers compared to control throughout the incubation period. During the initial days of incubation (upto 90 days), among the blended fertilizers, the NH_4 -N content was more in soils treated with biochar blended with urea in 1:2 ratio (B:U=1:2) increasing from 52.3 mg kg^{-1} at the 0th day to 115.7 mg kg^{-1} at 90 days, thereafter showing a gradual decrease, whereas in soils blended with biochar: urea in 1:1 ratio the increasing trend in the ammoniacal nitrogen release was prolonged upto the 180th day, reaching a maximum of 117.6 mg kg^{-1} , thereafter showing a decline. From 150 to 210 days after incubation ammoniacal nitrogen was significantly higher for biochar: urea in 1:1(Fig 2). The prolonged and sustained release of nitrogen from the biochar/ biochar-bentonite blended fertilizers, might be due to the initial adsorption of the fertilizers by biochar/ biochar-bentonite. The decrease in NH_4^+ -N content in soils for the

different treatments after reaching a maximum value might be due to the re-adsorption of NH_4^+ -N on the biochar/ biochar bentonite or soil surface. Similar trends were also reported by Jabin and Rani [12]. Since biochar can assist with the mineralization of nitrogen from applied fertilizer, the amount of ammoniacal nitrogen in soil treated with biochar could be higher than that of untreated soils [13]. As opposed to soils treated with urea alone, where NH_4^+ -N retention is mostly a result of hydrogen bonding and electrostatic interaction, the surface of biochar contains functional groups such as $-\text{COO}^-$ ($-\text{COOH}$), amino, and $-\text{O}(-\text{OH})$ that might be responsible for the strong retention and sustained release of ammoniacal nitrogen [14,15].

The NH_4^+ -N release of soils treated with biochar-bentonite: urea showed a gradual increase up to 240 days, thereafter showing a slight decrease. Blending of urea with biochar-bentonite in the ratio 1:0.5 and 1:1 gave maximum NH_4^+ -N release at 240 days, whereas in the blended fertilizer 1:2, the maximum release was at the 150th day. The sustainability of biochar-bentonite blended fertilizers was more than that of biochar blended fertilizers even though the value was higher for biochar blended fertilizers during initial days (Fig 3).

The ammoniacal nitrogen release from B:U at 1:1 ratio in sandy soil showed a maximum of approximately 80% increase compared to absolute control at 180 days of incubation. The biochar blended fertilizers showed sustained release of nutrients from soils. At the 0th day, percentage increase in NH_4 -N release from soils treated with biochar blended urea fertilizers ranged from 8-16% while the soil treated with urea alone showed a 46% increase compared to control.

Compared to soils treated with biochar/ biochar-bentonite blended urea fertilizer treatments, NH_4^+ release from soil treated with urea alone was rapid and reached a maximum at the 30th day ($115.73 \text{ mg kg}^{-1}$), thereafter showing a sharp decline till the 60th day, then maintaining a low value till the end of incubation. The NH_4^+ and NO_3^- adsorbed on biochar can be made available for microbial use, thus temporarily reducing its availability [4]. The ability of biochar molecule to retain NH_4^+ -N followed by its mineralization, causing an alteration from organic to inorganic form over time, may be the cause of the fluctuation in the trend of NH_4^+ -N detected during the incubation period. Compared to the urea fertilizer alone treatment, a smaller amount of NH_4^+ -N was released from biochar and biochar bentonite blended urea during the initial period of incubation. This might be due to the adsorption of ammonium to the negatively charged surface functional (CO-stretch) groups of biochar [16]. This can also be linked with the CEC of biochar as suggested by Rajkumar [17], who reported that 2880 positively charged NH_4^+ -N can be adsorbed and retained by one kilogram of coconut husk biochar having a CEC of $15.78 \text{ cmol (+) kg}^{-1}$.

Table 1: Effect of treatments on ammoniacal nitrogen content at different periods of incubation in sandy soil, mg kg⁻¹

Treatments	0 th	15 th	30 th	60 th	90 th	120 th	150 th	180 th	210 th	240 th	270 th	300 th	330 th	360 th
T ₁ - Absolute control	44.8	50.4	52.3	54.1	57.8	61.6	67.2	65.3	57.9	54.1	52.3	48.5	44.8	39.2
T ₂ - Soil + Biochar	48.5	52.3	56.0	65.3	72.8	74.6	76.5	72.8	70.9	69.1	65.3	61.6	52.3	46.6
T ₃ -Soil + Biochar-bentonite	46.6	50.4	57.8	61.6	67.2	70.9	72.8	74.6	78.4	74.6	72.8	70.9	65.3	61.6
T ₄ -Soil+ Biochar- Urea 1:0.5	48.5	61.6	67.2	78.4	84.0	95.2	100.8	97.1	98.9	95.2	84.0	80.3	74.6	70.9
T ₅ - Soil + Biochar- Urea 1:1	50.4	65.3	69.1	80.3	89.6	97.1	112.0	117.6	108.3	98.9	89.6	85.9	80.3	76.5
T ₆ -Soil +Biochar-Urea 1:2	52.3	70.9	89.6	100.8	115.7	106.4	95.2	89.6	87.7	84.0	82.1	78.4	70.9	59.7
T ₇ - Soil + Biochar- Bentonite: Urea 1:0.5	48.5	52.3	65.3	74.6	76.5	80.3	85.9	91.5	93.3	95.2	93.3	91.5	82.1	78.4
T ₈ - Soil + Biochar- Bentonite: Urea 1:1	50.4	54.1	67.2	78.4	80.3	82.1	87.7	93.3	95.2	97.1	91.5	89.6	87.7	80.3
T ₉ - Soil + Biochar- Bentonite: Urea 1:2	50.4	56.0	70.9	84.0	85.9	91.5	93.3	91.5	89.6	87.7	84.0	80.3	76.5	70.9
T ₁₀ - Soil+Urea	65.3	98.9	115.7	70.4	69.4	68.3	67.9	66.5	64.3	60.5	58.3	55.3	53.2	50.4
CD (0.05)	9.488	12.750	11.094	7.076	6.517	8.018	6.362	8.531	8.671	10.028	7.888	8.065	10.735	9.556

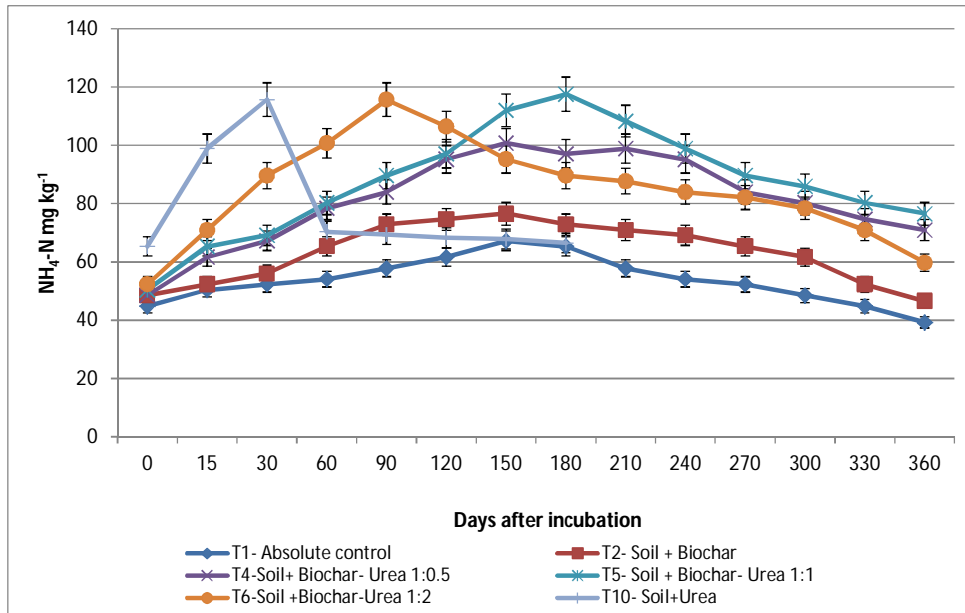


Fig 2: NH₄-N release from biochar and biochar blended urea fertilizers in sandy soils

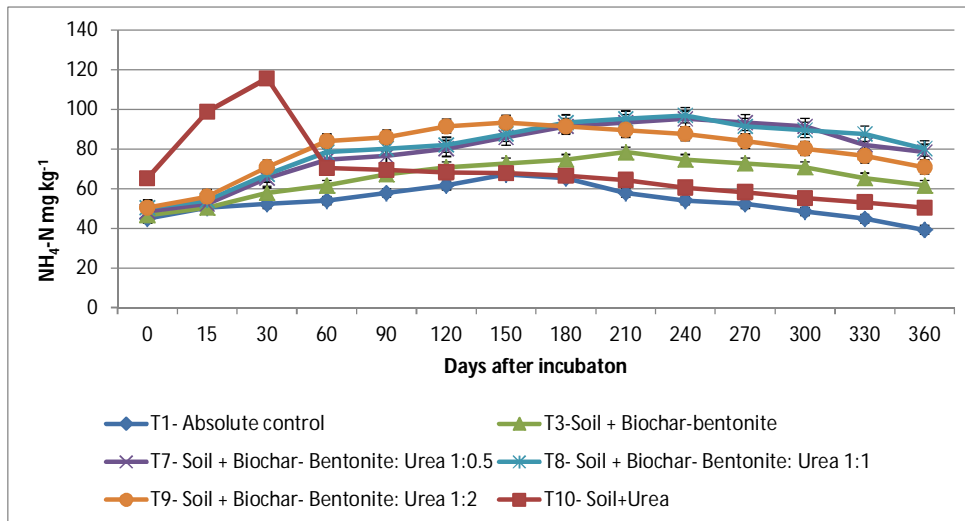


Fig 3: NH₄-N release from biochar- bentonite blended urea fertilizers in sandy soils

Release of nitrate nitrogen

The trend in the release of nitrate nitrogen from sandy soils on the addition of treatments is given in Table 2. Similar to ammoniacal nitrogen, the release of nitrate nitrogen showed an increasing trend during the initial days, thereafter showing a decrease which was comparatively less than that of NH_4^+ -N. Among the blended fertilizers, nitrate nitrogen was highest for biochar: urea in 1:2 (149.3 mg kg^{-1}) at 120 days, thereafter decreasing sharply, whereas for biochar: urea in 1:0.5 and 1:1 ratio, a gradual increase in release was noticed upto 150 days of incubation with a value of 140.0 and 151.2 mg kg^{-1} respectively thereafter showing a gradual decrease (Fig 3). But after the 150th day, biochar: urea in 1:1 retained its superiority in nitrate release upto 210 days (147.5 mg kg^{-1}). During the last months of incubation, the amount of nitrate nitrogen released from biochar-bentonite blended urea fertilizer was higher than that from biochar blended urea fertilizer (Fig 4). The decrease in nitrate nitrogen as the incubation period advanced after the peak release was comparatively less for biochar-bentonite blended urea fertilizers compared to the biochar blended fertilizers. On the 0th day, the percentage increase in NO_3^- -N release from the soil treated with biochar blended urea fertilizer ranged from 7-12% and that of soil treated with urea ranged from 19% compared to control.

The nitrate nitrogen release from soils treated with urea reached a maximum on the 30th day (149.3 mg kg^{-1}), and then showed a sharp decline till 60th day, thereafter maintaining a low value till the end of incubation. Higher nitrate nitrogen content was observed for the soil treated with biochar-bentonite: urea in 1:1 ratio from 240 to 360 days of incubation (Table 2, Fig 5).

Although the release of nitrate nitrogen from biochar bentonite blended fertilizers was more steady and sustained than the biochar blended fertilizers, the content was lower than that of biochar blended fertilizers due to the strong binding activity of bentonite. The content of nitrate nitrogen was more than that of ammoniacal nitrogen throughout the incubation period and this might be due to the conversion of NH_4^+ to NO_3^- on reaction with the biochar matrix. A similar release pattern was reported by Gwenzi [18] and Roy [19]. Biochar addition raises the population of nitrifying organisms resulting in increased production of nitrate nitrogen thus enhancing net nitrification [17, 20, 21]. Biochar addition also reduces soil temperature, boosts soil moisture and aeration thereby improving nitrifier activity [22]. Ye [23] pointed out that that a low ratio of fertilizer to biochar was preferable to fully utilize the potential of biochar for slow release and a high ratio of biochar to fertilizer results in a decline in the slow release efficiency due to pore structure, area and surface functional group limitations.

Table 2: Effect of treatments on nitrate nitrogen content at different periods of incubation in sandy soil, mg kg⁻¹

Treatments	0 th	15 th	30 th	60 th	90 th	120 th	150 th	180 th	210 th	240 th	270 th	300 th	330 th	360 th
T ₁ - Absolute control	78.4	85.9	89.6	91.5	98.9	100.8	102.7	98.9	95.2	91.5	82.1	78.4	74.6	72.8
T ₂ - Soil + Biochar	84.0	87.7	93.3	100.8	110.1	115.7	112.0	106.4	100.8	98.9	95.2	91.5	87.7	84.0
T ₃ -Soil + Biochar-bentonite	84.0	89.6	95.2	98.9	104.5	108.3	110.1	112.0	115.7	110.1	108.3	102.7	98.9	95.2
T ₄ -Soil+ Biochar- Urea 1:0.5	85.9	93.3	100.8	112.0	121.3	132.5	140.0	134.4	136.3	132.5	128.8	123.2	119.5	115.7
T ₅ - Soil + Biochar- Urea 1:1	85.9	95.2	104.5	117.6	123.2	138.1	151.2	145.6	147.5	136.3	132.5	126.9	121.3	117.6
T ₆ -Soil +Biochar-Urea 1:2	87.7	98.9	112.0	121.3	140.0	149.3	145.6	140.0	136.3	130.7	125.1	117.6	110.1	106.4
T ₇ - Soil + Biochar- Bentonite: Urea 1:0.5	84.0	91.5	98.9	110.1	117.6	123.2	140.0	138.1	140.0	138.1	136.3	130.7	126.9	119.5
T ₈ - Soil + Biochar- Bentonite: Urea 1:1	85.9	93.3	100.8	112.0	121.3	126.9	143.7	143.7	145.6	140.0	138.1	136.3	132.5	125.1
T ₉ - Soil + Biochar- Bentonite: Urea 1:2	87.7	97.1	108.3	119.6	134.4	147.5	138.1	130.7	128.8	121.3	117.6	110.1	106.4	102.7
T ₁₀ - Soil+ Urea	93.3	119.5	149.3	106.4	105.2	104.4	103.8	100.5	98.7	95.2	93.4	90.3	88.7	86.5
CD (0.05)	5.512	6.532	6.572	5.780	7.446	6.966	5.527	6.308	6.308	6.647	6.791	6.745	7.308	7.062

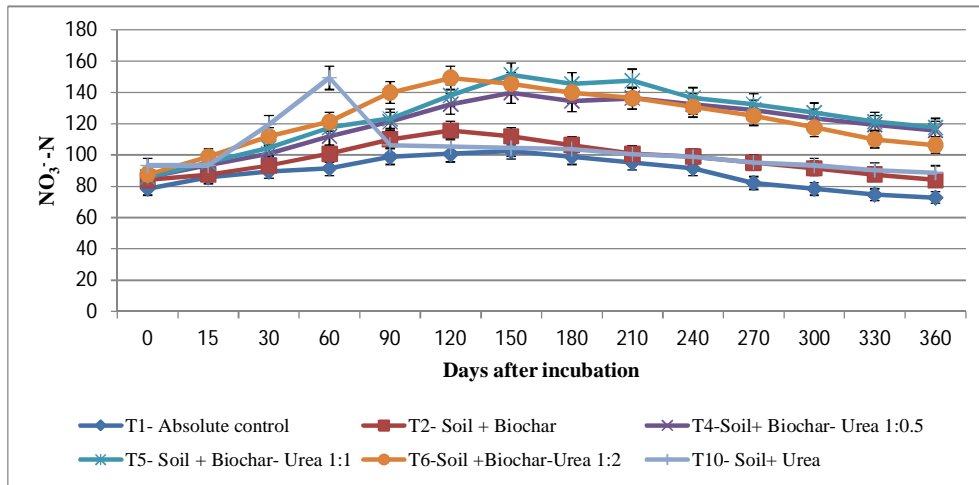


Fig 4: $\text{NO}_3^- \text{-N}$ release from biochar and biochar blended urea fertilizers in sandy soil

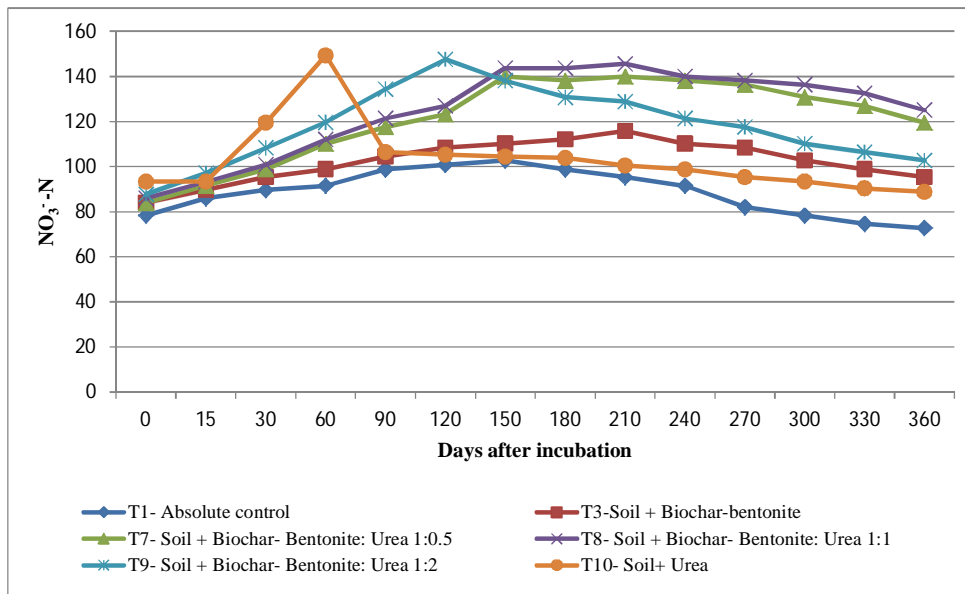


Fig 5: $\text{NO}_3^- \text{-N}$ release from biochar bentonite blended urea fertilizers in sandy soil

Conclusion

Blending of biochar with urea fertilizer resulted in a slow and steady release of ammoniacal and nitrate nitrogen compared to urea fertilizer alone. The rate of release of nitrate nitrogen was higher than that of ammoniacal nitrogen. Addition of bentonite enhanced both physical and chemical binding thereby slowing down the release of both NH_4^+ -N and NO_3^- -N thus increasing the period of sustained release. The incubation experiment in the laboratory may not accurately reflect field circumstances, but it does allow us to evaluate the nutrient release patterns from biochar and biochar-bentonite blended with urea at different ratios. Thus using biochar as a fertilizer carrier will slow down the release of nutrients into the soil, reduce fertilizer nutrient loss due to leaching, and increase the rate at which fertilizer nutrients are utilized. Based on the duration of the crop and its requirement, we can choose the appropriate ratio for blending biochar with urea fertilizer.

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Author's contribution-

Kavya- Conducted the lab study and performed the statistical analysis and wrote the first draft of manuscript

Dr. Rani- Corrected the manuscript