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Using ^{15}N Isotope to Evaluate the Effect of Brown Coal Application on the Nitrogen Fate in the Soil–Plant System

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Abstract: The problems of high nitrogen (N) fertilizer application rate and low N utilization efficiency are common worldwide in vegetable plantations. Application of brown coal (BC, also known as lignite) can increase crop yield and fertilizer N recovery efficiency (*NRE*). However, the effect of BC application on the utilization and distribution of exogenous N in the soil–plant system under different fertilization strategies is unclear. The pot experiment was set up in three factors of randomized design, including ^{15}N-labeled urea fertilizer, BC, and organic manure, and pakchoi was used as the test crop. There were five rates of ^{15}N-labeled urea, including 0, 100, 200, 300, and 400 kg N ha^{-1}, two rates of BC with 5 and 0 t ha^{-1}, and the organic manure with 0 t ha^{-1} which constitutes ten treatments. The other four treatments were the combination of one ^{15}N-labeled urea rate of 100 kg N ha^{-1}, two rates of BC with 5 and 0 t ha^{-1}, and two rates of organic manure with 100 and 0 kg N ha^{-1}. In conclusion, the interaction of all N fertilizer rates combined with BC improved soil ^{15}N retention efficiency by 10.14% compared without BC amendment. Between 200 and 300 kg N ha^{-1}, the average potential loss rate of ^{15}N decreased by 10.41%. The application of BC could reduce N loss by enhancing plant N uptake and increasing soil retention. The combined use of 200 kg N ha^{-1} fertilizer and 5 t ha^{-1} of BC would maintain a high fertilizer *NRE* and ensure pakchoi yield.

Keywords: brown coal; ^{15}N isotope; N fates; N recovery efficiency; N loss rate

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1. Introduction

Two major challenges facing global agriculture include improving nitrogen recovery efficiency (*NRE*) and reducing the widespread loss of soil organic matter. The nitrogen (N) is one of the most important limiting nutrients in vegetable production. However, N utilization is very low and the recovery rate of N from soil–plant systems rarely exceeds 50% of the applied fertilizer [1]. N loss from excessive N application causes a huge waste of resources and environmental burden [2]. N loss in agricultural production is mainly influenced by climate and soil conditions [3]. Soil organic matter provides many beneficial functions for crop production. The application of natural organic matter (OM) with high humic content and N fertilizers to crops can improve soil fertility, increase the duration of fertilization, enable more efficient nutrient uptake by crops, and reduce to some extent the environmental N losses due to excessive fertilizer application [4]. Brown coal (BC), also known as lignite, is an OM-rich humic acid-like substance [5], and the humic acids isolated from BC have similar chemical characteristics to those isolated from soil samples [6]. Some commercial humates are obtained from BC [7]. BC is generally a low-rank coal, widely distributed around the world, with reserves of about 500 billion tons [8]. BC has been shown to reduce ammonia emissions from animal manure composts and improve the final compost quality [9,10]. However, a unified understanding of the effects of BC application in agricultural soils needs to be improved. Scientific research indicated that by inhibiting urease activity [11] BC could reduce N leaching and N_2O emissions [12], increasing N effectiveness for plants. Moreover, BC is rich in complex microporous (0.4–1.2 nm) structure with a high specific surface area and many active sites [13]. The presence of carboxyl and phenolic functional groups makes BC easily complexed with metals or other cations (e.g., NH_4^+), which can significantly increase soil conductivity [14], stabilize heavy soil metals [15], reduce heavy metal uptake by crops [16], and enhance the absorption of phosphorous (P), iron (Fe), potassium (K), and other nutrient elements [17]. It will also improve soil water and moisture-holding capacity and permeability.

It has also been reported that low-order coal increases crop yield by improving soil biochemical properties, because the microbial activity of the soil affects the distribution and stability of N [18]; soil microbial activity also affects the stoichiometry, nutrient limitation, and N cycling [19,20]. Due to the acidic pH of BC, it may be an excellent organic additive or soil conditioner in alkaline soils [21]. However, soil health benefits of BC application strongly depend on the soil type, pasture species, and BC material and its application rate [22]. Tran et al. [23] reported that unprocessed BC had minor and temporary effects on soil microbial activity and community composition.

The effects of BC as a soil amendment to improve soil properties for plant yield and fertilizer efficiency have been well documented [5,24,25]. The effects of BC application with different N application rates and composts on exogenous N uptake in the plant–soil environment system have not been well studied, while this effect is crucial for increasing vegetable yields and developing environment-friendly fertilization programs. The ^{15}N labelling method is considered the only direct measure of N uptake from applied fertilizers and the most reliable method for tracking the flow and fate of N in the plant–soil system [26]. Therefore, this method has been widely used by many researchers [27–30]. We hypothesized that BC/BC compost could improve N use of pakchoi by increasing plant N uptake and soil retention. The adsorption of BC could delay the release of mineral N, thus maintaining N and synchronizing plant N demand and soil N supply. The ^{15}N tracing technique allows us to trace the whereabouts of N after its application to the soil and identify the source of N absorbed by the crop. The results of this experiment will provide theoretical support for further optimization of BC resources.

2. Materials and Methods

2.1. Experimental Site Overview and Experimental Design

The pot trial was conducted in a greenhouse shed from 12 October to 13 November 2018 (37°79′56″ S, 144°96′21″ E) at the Parkville campus of the University of Melbourne, Australia. The temperature in the greenhouse shed was maintained between 18 and 25 °C. The pakchoi variety *Brassica rapa* Var. *Chinensis* "Hei Xia F_1" was used as the test crop. The greenhouse temperature and humidity dynamics during the growing period are shown in Figure 1a.

The BC was Yallourn brown coal excavated from an open pit mine in the Latrobe Valley, Victoria, Australia, which was used primarily in a local power plant. Soil samples used in the experiments were obtained from a vegetable farm in Clyde, Victoria, Australia. The soils were classified as sandy loam, and inorganic fertilizers were applied individually for over four years before collecting soil samples. Topsoil samples of 0−15 cm were collected from the field, sieved through a 2 mm screen, and mixed thoroughly into the pots. The physical and chemical properties of the BC and soils used in this study were given in Table 1.

The experimental pots were polyvinyl chloride (PVC) buckets filled with a uniform mix of 4.87 kg of soil. The small holes at the bottom of the bucket were made to improve soil aeration. The experiment consisted of five N rates, 0, 100, 200, 300, and 400 kg N ha^{-1} of urea (0, 0.5014, 1.0083, 1.5125, and 2.0164 g pot^{-1}, respectively, estimated by dry mass of 0–15 cm topsoil at 2.10 million kg ha^{-1}). The ^{15}N-labeled urea was obtained from the Shanghai Research Institute of Chemical Industry, with an abundance value of 10.10%, containing 464 g kg^{-1} of N. BC levels of 0 and 5 t ha^{-1} (0 and 15.37 g dry BC pot^{-1}, respectively). In addition, the organic manure combination treatment was set up combining 0 and 100 kg N ha^{-1} urea with 0 and 5 t ha^{-1} BC at the level of 100 kg N ha^{-1} organic manure. A total of 14 treatments with 5 replicates were adopted in the experiment, and 70 pots were placed in a randomized arrangement.

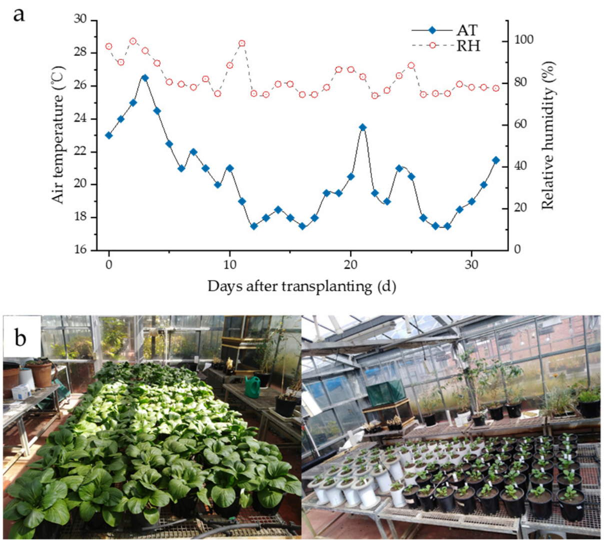

Figure 1. Experimental layout: a. Dynamics of air temperature (AT) and relative humidity (RH) in the greenhouse shed; b. Pot arrangement at the greenhouse shed, on harvest (**left**) and after transplanting during 3–4 leaf age (**right**).

Table 1. Physical and chemical properties of brown coal (BC), organic manure and sandy loam soil.

Material	BC	Sandy Loam	Organic Manure
pH (1:5H_2O)	4.13	7.19	7.95
Total C [(a)] (g kg^{-1})	604.0	37.5	196.0
Total N [(b)] (g kg^{-1})	4.9	4.3	7.1
C:N [(c)]	123.3	8.72	27.2
NO_3^--N (mg kg^{-1})	trace	50.0	43.2
NH_4^+-N (mg kg^{-1})	trace	8.63	46.0
CEC [(d)] (Cmol kg^{-1})	19.9	—[(e)]	—
P (g kg^{-1})	0.10	0.05	—
K (g kg^{-1})	0.04	0.09	—
S (g kg^{-1})	1.99	0.03	—
Ca (g kg^{-1})	0.72	0.80	—
Mg (g kg^{-1})	1.42	0.04	—
Cu (mg kg^{-1})	<1	—	—
Zn (mg kg^{-1})	3.7	—	—
Mn (mg kg^{-1})	42.0	—	—

Note: (a) total carbon; (b) total nitrogen; (c) the ratio of total carbon to total nitrogen; (d) cation-exchange capacity; (e)—indicates no measurement.

The P and K fertilizers were all identical while the N application rate varied among the treatments. Superphosphate was used at an application rate of 90 kg ha^{-1}, and potassium chloride was used at an application rate of 180 kg ha^{-1}. Both the P and K fertilizers were completely used as basal doses with one-third of the N fertilizers as the basis, and the rest were follow-up applications on the 7th and 17th days of planting in equal amounts, respectively. For treatments containing organic manure, chicken manure compost (70.68 g pot^{-1}) was applied to the potted soil as base fertilizer. The experimental treatments are shown in Table 2.

Table 2. Experimental treatment design.

Treatment	Urea kg N ha^{-1}	BC t ha^{-1}	Organic Manure kg N ha^{-1}
$N_0B_0F_0$	0	0	0
$N_1B_0F_0$	100	0	0
$N_2B_0F_0$	200	0	0
$N_3B_0F_0$	300	0	0
$N_4B_0F_0$	400	0	0
$N_0B_1F_0$	0	5	0
$N_1B_1F_0$	100	5	0
$N_2B_1F_0$	200	5	0
$N_3B_1F_0$	300	5	0
$N_4B_1F_0$	400	5	0
$N_0B_0F_1$	0	0	100
$N_0B_1F_1$	0	5	100
$N_1B_0F_1$	100	0	100
$N_1B_1F_1$	100	5	100

Note: N_0, N_1, N_2, N_3, and N_4 represent the N content fertilizer rate at 0, 100, 200, 300, and 400 kg N ha^{-1}, respectively; B_0 and B_1 represent BC application rates of 0 and 5 t ha^{-1}, respectively. F_0 and F_1 represent organic manure rates of 0 and 100 kg N ha^{-1}, respectively.

The BC, urea and organic fertilizer were well mixed and applied to the potting soil as a base fertilizer. Afterward, two 3–4 leaf pakchoi seedlings were transplanted into each pot on 12 October 2018. The soil water content of the potted plants was measured by weighing method. The irrigation amount was applied every 2 to 3 days according to evaporation so that the soil water content was adjusted to 90% of the field capacity (236.7 g kg^{-1}). Table 3 showed the natural abundance of ^{15}N during the experiment, measured from the control treatment without additions of urea and BC. Figure 1b was the experimental arrangement.

Table 3. The natural abundance of ^{15}N during the pot experiment.

Material ^{15}N Abundance	Natural Abundance of ^{15}N in Plants [(a)]	Natural Abundance of ^{15}N in Soils [(a)]	Fertilizer ^{15}N Abundance [(b)]
Abundance value (%)	0.4140	0.3483	10.10

Note: (a) The natural abundance of ^{15}N in plants and soils was measured empirically based on N_0B_0 treatment. (b) Fertilizer ^{15}N abundance is provided by the manufacturer.

2.2. Sample Collection and Determination

2.2.1. Determination of Biomass of Different Parts of Pakchoi

Pakchoi was harvested on the 32nd day after transplanting and its biomass was determined, including the fresh mass of aboveground and belowground (root system). A small portion of the leaves was taken to determine nitrate-N, and most of the plant samples were dried in an oven at 105 °C for 20 min and then adjusted to 75 °C until the samples were dried to a constant mass and were used to determine the dry matter mass.

2.2.2. Soil Mineral N Determination

On the day of pakchoi harvesting potted soil samples were taken uniformly from the greenhouse with sealed bags and transported to the laboratory for cryopreservation via ice box storage. In the laboratory, 5 g of fresh soil was added to 50 mL of 2 mol L^{-1} KCL solution to extract mineral N (NH_4^+ and NO_3^-). After 1 h of shaking at constant room temperature of 20–25 °C, the samples were filtered through filter paper and collected, and the NH_4^+ and NO_3^- in the solution were determined using a continuous flow analyzer. (Skalar SAN++, Breda, The Netherlands)

2.2.3. Determination of ^{15}N Atomic Percentage of Soil and Crops

Soil and crop samples were grounded and passed through a 0.15 mm sieve and analyzed by a stable isotope ratio mass spectrometer (Thermo Fisher Scientific Delta V Advantage, Waltham, Massachusetts, USA) and elemental analyzer (Thermo Fisher Scientific Flash 2000 HT, Waltham, Massachusetts, USA) to determine the percentage of ^{15}N atoms in each part of the crop and soil samples.

2.2.4. Soil and Plant Carbon and N Determination

After harvesting the soil in each bucket was thoroughly mixed and then 100 g samples were collected and air-dried. Residual roots and small stones were carefully removed with forceps to take a partial soil subsample after removal. Soil and crop organic C contents were measured using the potassium dichromate oxidation method. Soil and crop total N (TN) were measured using the Dumas combustion method. An amount of 0.2 g of soil and crop samples were weighed in N-free tin foil, squeezed out of the air and placed in an autosampler. The sample was fully combusted in the oxidation tube, and the generated gas was detected by a thermal conductivity detector with the reaction conditions: combustion tube temperature of 990 °C and reduction tube temperature of 650 °C.

2.3. Data Analysis

To evaluate N utilization and conversion we followed Wang and calculated [31] apparent fertilizer N recovery efficiency (*NRE*), N derived from fertilizer (*Ndff*), plant ^{15}N recovery ($^{15}N_{recovery}$), soil ^{15}N retention ($^{15}N_{retention}$), plant ^{15}N recovery efficiency (^{15}NRE), soil ^{15}N retention efficiency ($^{15}NRE_{soil}$), and potential ^{15}N loss efficiency (^{15}NLE).

2.3.1. Apparent fertilizer *NRE* Was Shown in the Equation Below (Equation (1))

$$NRE = \frac{\Delta N_{\text{uptake}}}{N_{\text{fertilizer rate}}} \tag{1}$$

where ΔN_{uptake} (g pot^{-1}) is the difference between the total N uptake of plants with added labeled urea and the control plants. $N_{\text{fertilizer rate}}$ (g pot^{-1}) included the N per pot from applied urea and organic manure.

2.3.2. N Derived from Fertilizer (Equation (2))

$$Ndff = \frac{^{15}N_{lx} - ^{15}N_{\text{natural}}}{^{15}N_{l} - ^{15}N_{\text{natural}}} \tag{2}$$

where $^{15}N_{lx}$ is the ^{15}N abundance of samples which can be plant organs or soil (%). When the samples were plant leaves, roots and soil, the *Ndff* expressed as $Ndff-_{\text{leaf}}$, $Ndff-_{\text{root}}$ and $Ndff-_{\text{soil}}$, respectively. $^{15}N_l$ is the ^{15}N abundance of labeled urea (%), $^{15}N_{\text{natural}}$ is the natural abundance of ^{15}N in soils or plants (%).

2.3.3. The Amount of Labeled Urea Absorbed by the Plant ^{15}N Recovery (g pot^{-1}) Was Calculated Using the Following Equation (Equation (3))

$$^{15}N_{\text{recovery}} = N_{\text{plant}} \times \frac{^{15}N_{lp} - ^{15}N_{\text{natural}}}{^{15}N_{l} - ^{15}N_{\text{natural}}} \tag{3}$$

where N_{plant} and $^{15}N_{lp}$ are the total N uptake (g pot^{-1}) and ^{15}N abundance of plant samples (%), respectively. The plant included leaf and root parts, which were counted separately.

2.3.4. The Amount of Labeled Urea Retained in the Soil ^{15}N Retention (g pot^{-1}) Was Calculated Using the Following Equation (Equation (4))

$$^{15}N_{\text{retention}} = N_{\text{soil}} \times \frac{N_{ls} -^{15} N_{\text{natural}}}{^{15}N_{l}^{-15}N_{\text{natural}}} \tag{4}$$

where N_{soil} and $^{15}N_{ls}$ are the amount of total N in soil (g pot^{-1}) and ^{15}N abundance of soil samples (%), respectively.

2.3.5. Plant ^{15}N Recovery Efficiency (Equation (5))

$$^{15}NRE = \frac{^{15}N_{\text{recovery}}}{^{15}N_{\text{fertilizer rate}}} \tag{5}$$

where the $^{15}N_{\text{fertilizer rate}}$ is the amount of applied labeled urea (g pot^{-1}).

2.3.6. Soil ^{15}N Retention Efficiency (Equation (6))

$$^{15}NRE_{\text{soil}} = \frac{^{15}N_{\text{retention}}}{^{15}N_{\text{fettilizer rate}}} \tag{6}$$

2.3.7. Potential ^{15}N Loss Efficiency (Equation (7))

$$^{15}NLE = 1 -^{15} NRE -^{15} NRE_{-soil} \tag{7}$$

2.4. Statistical Analysis

All data were analyzed by SPSS 25.0 software (SPSS Inc., Chicago, IL, USA). Analysis of variance (ANOVA) was used to examine differences between the BC amendment and ^{15}N-labeled urea treatments and organic manure treatments, as well as their interactions. The differences between all the treatments were detected using Duncan's multiple-range test at $p < 0.05$. Correlation analysis is used to measure the intensity and direction of the correlation between multiple indicators. The figures were generated by Origin 2021 and PowerPoint 2019 software (Origin Lab Corp., Microsoft Corp., Redmond, MA, USA).

3. Results and Discussions

3.1. Dry mass and N Uptake in Aboveground Parts of Pakchoi

The results of leaf nitrate-N (NO_3^-), leaf dry mass, ^{15}N, TN uptake, and *Ndff* in the leaf (*Ndff*$-_{\text{leaf}}$) are shown in Figure 2. Leaf dry mass of pakchoi showed an overall trend of initial increasing and then decreasing with the increase in N application, with the highest aboveground biomass at the 200 kg N ha^{-1} level and combined with BC treatment at 5 t ha^{-1}. The aboveground dry mass did not significantly increase at the 100 kg N ha^{-1}, 200 kg N ha^{-1} and 300 kg N ha^{-1} levels due to the addition of BC, while in the non-BC application there was a small increase in aboveground dry mass at the 200 kg N ha^{-1} level. Aboveground urea N uptake, total N uptake, and inorganic fertilizer contribution of pakchoi were all highly correlated with N application, and all increased with the increase in urea N application rate. In particular, when the N application rate was 200 kg N ha^{-1}, the *Ndff*$-_{\text{leaf}}$ value from urea N in non-BC and BC treatment reached 49.77% and 50.90%, respectively. When the N application rate was lower than 200 kg N ha^{-1}, the source of N uptake by pakchoi was mainly from the soil N pool. With the increase in N application rate the *Ndff*$-_{\text{leaf}}$ value kept rising, and the N uptake gravity center from native soil pool shifted to exogenous urea N. It can be assumed that the dependence of pakchoi on the native soil N pool gradually decreased with the application of exogenous N. Although the leaf dry mass and urea contribution indexes were not significantly influenced by BC, they slightly increased compared with non-BC application ($p > 0.05$). The leaf NO_3^- was significantly correlated with all factors and increased with the increase on urea application rate. In comparison, BC application improved leaf NO_3^- enrichment in this process with an average increase of 9.97% ($p < 0.05$) at all urea levels. In contrast, organic manure application decreased leaf NO_3^- by 31.13% ($p < 0.01$).

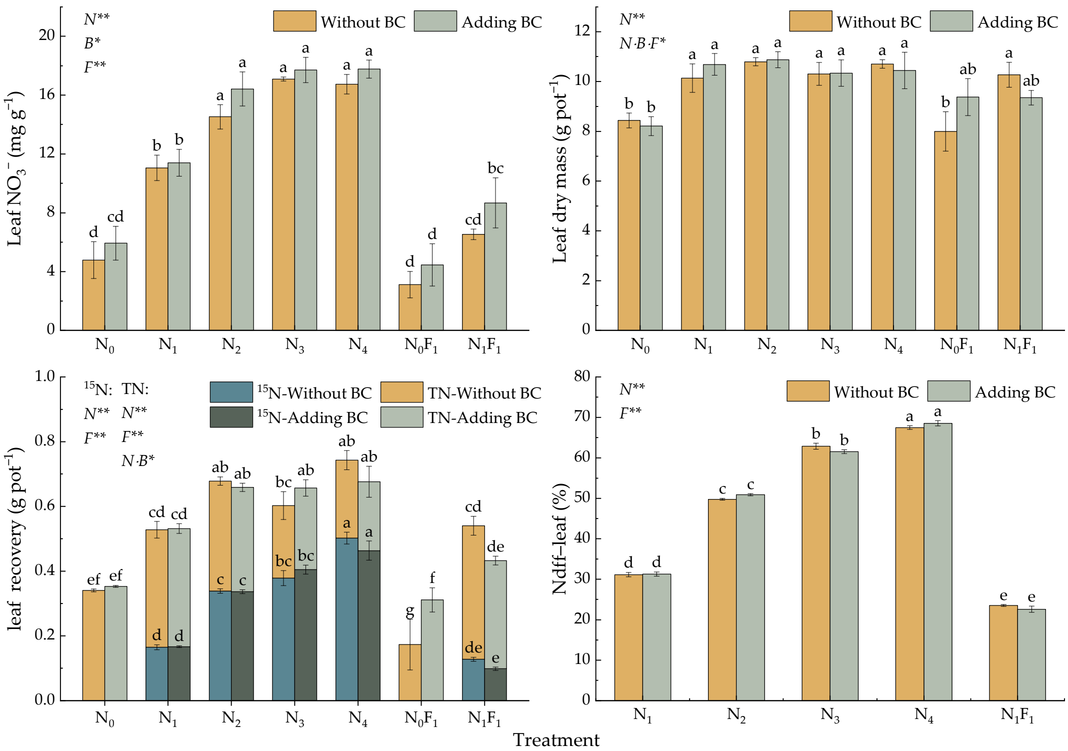

Figure 2. Leaf NO_3^-, Dry mass, $^{15}N_{recovery}$ and its proportion. Note: Vertical bars represent standard errors of the means (n = 5). Different letters represent statistical class among the treatments at $p < 0.05$, and the presence of means with the same letter is not significantly different. Source of variation, N = ^{15}N-labeled urea; B = brown coal; F = organic manure. * and ** indicate significant differences at $p < 0.05$ and $p < 0.01$, respectively. N_0, N_1, N_2, N_3, and N_4 represent the urea application rate, 0, 100, 200, 300, and 400 kg N ha^{-1}, respectively. F_1 represents organic manure of 100 kg N ha^{-1}.

Previous studies have shown that humus BC pelletized urea (BCU) increased rape biomass and wheat protein content compared with urea applied in equal amounts of N [24], while BC-coated slow-release urea had a retarding effect on maize growth, but maize seed number and yield in humic acid-containing urea at the end of growth exceeded those of applied regular urea [32]. In contrast, there was no significant effect of BC combined with urea on the dry mass of pakchoi ($p > 0.05$). The effect of yield increase with BC application was not significant, which could be due to the nature of the selected BC itself, or likely because of the low content of water-soluble humic acid in its natural state, or the dried and crushed sieve processing of BC in this experiment without activation (oxidation) treatment which may not be easily utilized by humic acid. On the other hand, it maybe because the porous physical adsorption nature of the BC surface [24], which to some extent absorbs nutrients, resulting in an insignificant yield increase in pakchoi at this BC-dispensing level. It was also reported that the actual effects of the amendment would vary for different BCs, crop types, soils, and environmental conditions [33]. The results of this experiment also showed that there was a suitable range for the amount of urea and excessive application of N exerted adverse effects. The aboveground dry mass of pakchoi showed a trend of increasing and then decreasing trend with the increase in N application, and N application had a highly significant effect on biomass ($p < 0.01$), which is consistent with the results of earlier findings [34].

It is reasonable to speculate that although the increase in N application can increase crop yield, there is an upper limit for the crop N requirements. The proportion of N obtained by the plant from the soil decreases at high N application levels. Excessive fertilizer N that could not be absorbed and deposited in the soil except for N loss, resulted in soil acidification over time. Compared with $N_0B_0F_0$ treatment without N application, the average dry yield increased by 1.7, 0.65, −0.49, and 0.4 g plant^{-1} in $N_1B_0F_0$, $N_2B_0F_0$, $N_3B_0F_0$, $N_4B_0F_0$, respectively, resulting in reduced marginal benefit and N waste. The N application rate for the higher-yielding treatment in this trial was 200 kg N ha^{-1}. If the 200 kg N ha^{-1} was used as a guide for fertilizer application, the contribution of the original soil N pool and exogenous urea to plant growth would be more or less equal, and the N in the soil could be better utilized, thus reducing the dependence of plants on chemical fertilizers. The BC amendment with 200 kg N ha^{-1} also increased the uptake and utilization of N, resulting in a 2.28% increase in $Ndff{-}_{\mathrm{leaf}}$ compared with 200 kg N ha^{-1} without BC treatment ($p > 0.05$).

3.2. Dry Mass and N Uptake of Pakchoi Roots

The results of root dry mass, root crown ratio (RSR), root $^{15}N_{recovery}$, and *Ndff* in root ($Ndff{-}_{\mathrm{root}}$) were calculated. The results (Figure 3) showed that root dry mass and RSR were significantly influenced by the applied N level. The root dry mass gradually decreased with the increase in N application rate, averaging 33.17% ($p < 0.01$) at the four N application levels of urea, 25.15% ($p < 0.01$) at the four N application levels of BC addition, and 7.47% ($p > 0.05$) at the 100 kg N ha^{-1} level for the treatments with organic manure addition. RSR also decreased with the N application level, which indicated that a high dose of N application reduced the developmental potential of pakchoi roots and made a tendency to distribute dry matter to the aboveground part. It also showed by the decrease in total N uptake by the root system, but this decrease had a lower limit and the rate of decline gradually slowed down after 100 kg N ha^{-1} until the N uptake by the root system in a single pot was stabilized at about 0.016 g. Notably, although the root TN uptake decreased, the root $^{15}N_{recovery}$ system increased with the increase in N application rate, as verified by the increase in $Ndff{-}_{\mathrm{root}}$ which increased by 60.53%, 33.56%, and 7.46% for additional 100 kg of urea applied from 100 kg ha^{-1} ($p < 0.01$). This gradually decreasing dependence on the original soil N pool was consistent with the aboveground performance. This effect was enhanced by the addition of BC. Multifactorial analysis showed that combined urea–BC had a significant effect on urea contribution. The addition of BC increased urea $Ndff{-}_{\mathrm{root}}$ by 0.38%, 1.99%, and 2.28% at the urea rates of 100, 200 and 400 kg N ha^{-1}, respectively ($p > 0.05$).

3.3. Retention and Soil N Transformation

The results of soil mineral N, C:N ratio (C:N), $^{15}N_{retention}$, and $Ndff{-}_{\mathrm{soil}}$ calculations are shown in Figure 4. The results indicate that soil nitrate (NO_3^-) content increased with the increase in N application levels. Applying BC or organic manure also significantly increased the soil NO_3^- level. The BC application increased soil NO_3^- content by 40.29%, 1.92%, 39.39%, and 0.77% at 400, 300, 200 and 0 kg N ha^{-1} rates, respectively ($p < 0.01$). In contrast, the BC application reduced the soil NH_4^+ content by an average of 3.86% at the same urea level, especially in the control treatment, with the maximum decrease of 12.41%, but this effect was not significant ($p > 0.05$). The soil NH_4^+ content was kept stable at about 4 mg kg^{-1} at all treatments.

With the increase in N application rate, compared to the control group the soil C:N gradually decreased by 5.51%, 5.92%, 14.14%, and 18.82% at the rates of 100, 200, 300, 400 kg N ha^{-1} with non–BC application, and decreased by 3.14%, 3.72%, 15.05%, and 16.63% with BC application, respectively. The application of BC or organic manure increased soil C:N at the same level of N application, with an average of 5.04% ($p < 0.01$) in the treatment of BC application, the effect of which was greater than that of 1.98% ($p > 0.05$) with organic manure application. The increase in N application and organic manure application significantly increased $^{15}N_{retention}$. Furthermore, BC application also increased $^{15}N_{retention}$ by 10.72%, 5.95%, 20.35%, and 16.08% at the rates of 100, 200, 300 and 400 kg N ha^{-1}, respectively. With the increase in urea application rate, the *Ndff*–$_{soil}$ increased ($p < 0.01$). Compared with the non–BC group, *Ndff*–$_{soil}$ in the treatments under BC application increased by 3.33%, 19.04%, and 16.65% ($p < 0.05$) at the rates of 200, 300, and 400 kg N ha^{-1}, respectively. This indicated that BC application increased the proportion of exogenous urea in the soil.

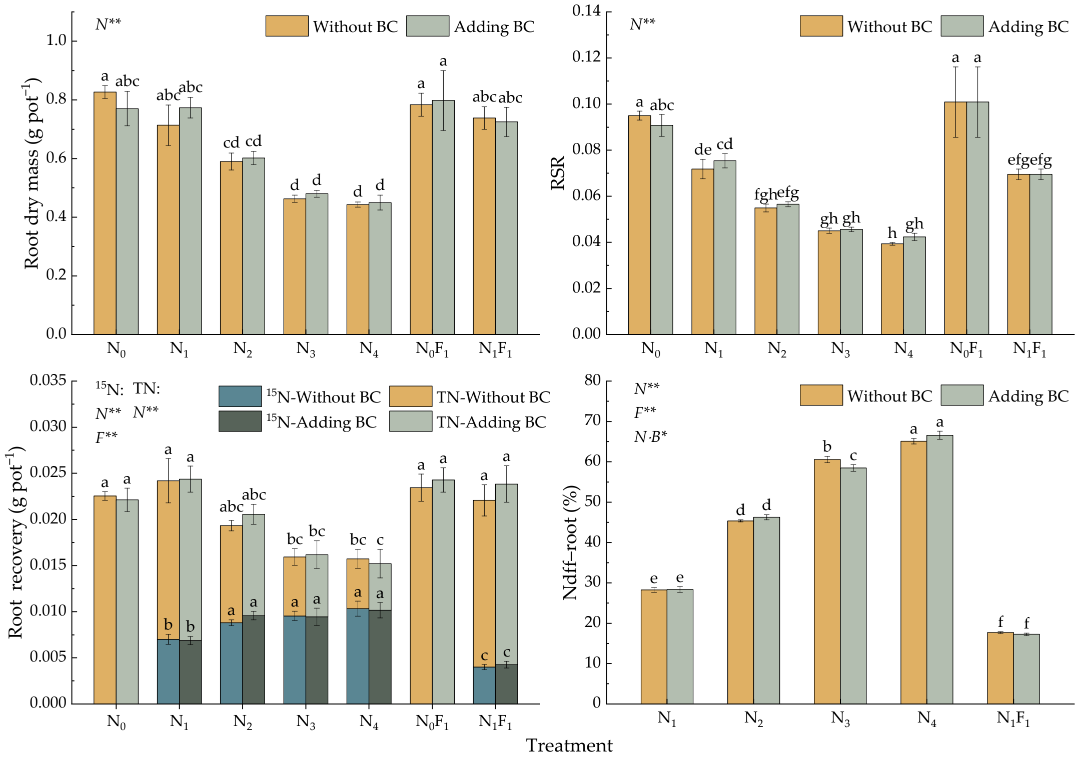

Figure 3. Root dry mass, RSR, $^{15}N_{recovery}$, and its proportion. Note: RSR means root crown ratio. Vertical bars represent standard errors of the means (n = 5). Different letters represent statistical class among the treatments at $p < 0.05$, and the presence of means with the same letter is not significantly different. Source of variation, N = ^{15}N-labeled urea; B = brown coal; F = organic manure. * and ** indicate significant differences at $p < 0.05$ and $p < 0.01$, respectively. N_0, N_1, N_2, N_3, and N_4 represent the urea application rate, 0, 100, 200, 300, and 400 kg N ha^{-1}, respectively. F_1 represents organic manure of 100 kg N ha^{-1}.

The soil NO_3^- content increased with the increase in N application, which was in agreement with previous work [35], and the soil NH_4^+ also gradually increased to about 4 mg kg^{-1}. The results of the univariate analysis showed that there was an extremely significant effect of BC application on soil NO_3^- content ($p < 0.01$). The two-way interaction between urea N and BC application had a highly significant effect on soil NO_3^- content ($p < 0.01$). This may be due to the absorption of BC to N, which provides energy and suitable habitat for microbial growth and reproduction. There is direct [36] and indirect [37] evidence that BC has a positive effect on the growth of soil microorganisms. Therefore, it is believed that soils with BC addition, ammonifying microorganisms, and nitrifying bacteria obtained a suitable environment and substrate for rapid reproduction. Additionally, microbial activity was enhanced [38], accelerating mineralization and nitrification, and soils with BC application produced and released more NO_3^-. BC reduced exogenous urea losses in the process, thus increasing the soil inorganic N pool. The rich oxygen-containing functional groups and lower pH of BC made it more suitable for neutral and alkaline soils because the rich functional groups posed a high cation-exchange capacity

(CEC). The higher CEC led to higher NH_4^+ retention and lower leaching of NO_3^- [39]. Moreover, the high porosity of BC enhanced its ability to adsorb nutrient ions on porous surfaces [40]. It has been shown that the adsorption capacity of BC was more than twice that of activated-C prepared from coconut shells [41]. In this experiment, the $Ndff-_{soil}$ treated with BC was increased compared with that treated with urea alone ($p < 0.05$), probably due to the increased retention of N in soil by BC adsorption of exogenous urea. In addition, the results of this experiment showed that the dosed BC had a highly significant effect on increasing soil C:N. This effect was positive for plant growth because ammonia N may be abiotically immobilized on humic acid when the C:N was higher than 10 [42]. For these reasons, treatments with BC increased the ability of the soil to provide N compared with urea N alone, making more N available for crop uptake. When the C:N of soil matrix was between 1 and 15, mineralization and N release would occur rapidly, which was conducive to N uptake by crops. The lower the C:N was, the faster the N released and the greater proportion of N loss. The C:N was an equilibrium state with the ratio between 20 and 30. When the C:N was greater than 35 the mobilization of microorganisms was promoted [43]. Therefore, too high or too low C:N was not conducive to the distribution of N to crops. As the soil foundation C:N was generally lower than 10, application of organic materials with high C:N to the soil, such as straw, biochar and lignite, would be an effective practice to maintain good C:N in the soil. Moreover, in this single crop season, BC application increased soil C:N by 5.04% on average. According to the rate of BC application in this experiment, it is unlikely to exceed the appropriate range for a certain period and will have a positive impact on crop growth.

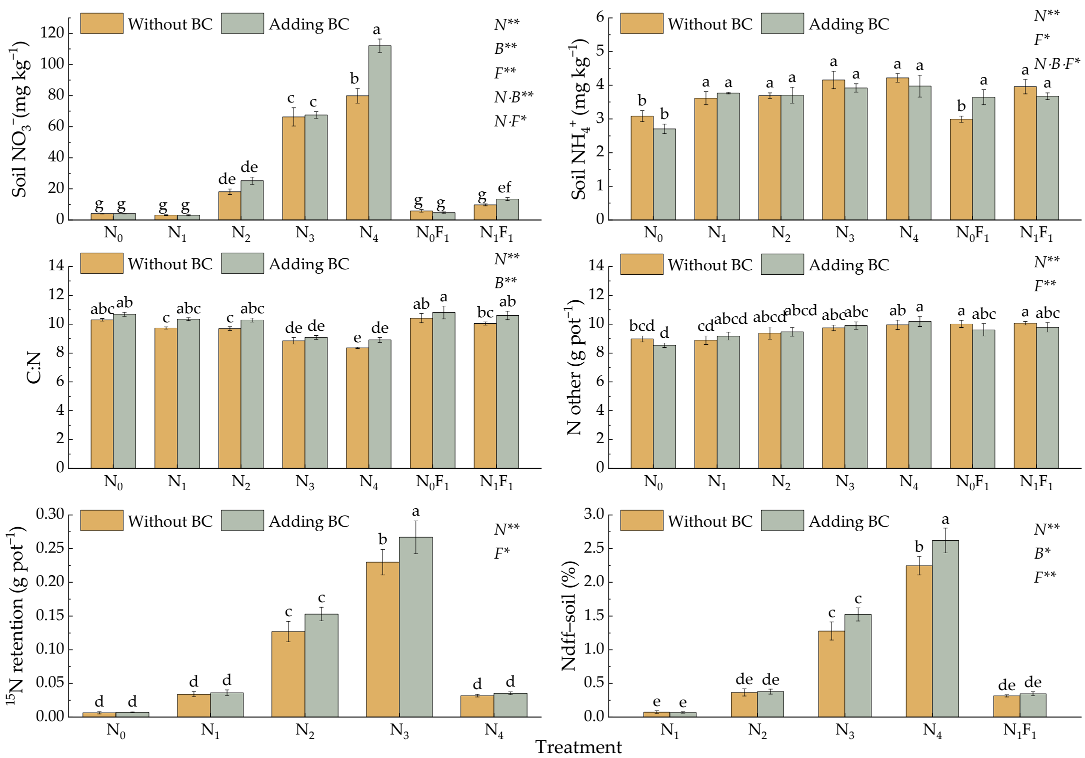

Figure 4. Soil mineral N, C:N, $^{15}N_{retention}$ and its proportion. Note: C:N means the ratio of total carbon to total nitrogen in soil. Vertical bars represent standard errors of the means (n = 5). Different letters represent statistical class among the treatments at $p < 0.05$, and the presence of means with the same letter is not significantly different. Source of variation, N = ^{15}N-labeled urea; B = brown coal; F = organic manure. * and ** indicate significant differences at $p < 0.05$ and $p < 0.01$, respectively. N_0, N_1, N_2, N_3, and N_4 represent the urea application rate, 0, 100, 200, 300, and 400 kg N ha^{-1}, respectively. F_1 represents organic manure of 100 kg N ha^{-1}.

3.4. Effect of Combined Application of BC on Utilization and Distribution of Urea Nitrogen

The results of the one-way ANOVA showed that *NRE* was highly affected by the level of N supply (Figure 5). When urea application rate was 100 kg N ha^{-1}, the maximum *NRE* was more than 90%. The *NRE* quickly decreased to about 40% and tended to be stable as the level of applied N increased. Compared with the urea application of 100 kg N ha^{-1}, the *NRE* at the rates of 200, 300, and 400 kg N ha^{-1} decreased by 21.16%, 54.53%, and 56.86% ($p < 0.01$). Compared with the urea application of 100 kg N ha^{-1} + 5 t ha^{-1}, the *NRE* under the treatments with BC reduced by 24.51%, 54.07%, and 60.80%, respectively ($p < 0.01$). The greatest loss of *NRE* occurred as urea N rate increased from 200 to 300 kg N ha^{-1}. Compared with $N_1B_0F_1$ treatment, the *NRE* under $N_1B_1F_1$ reduced significantly by 53.70% ($p < 0.01$).

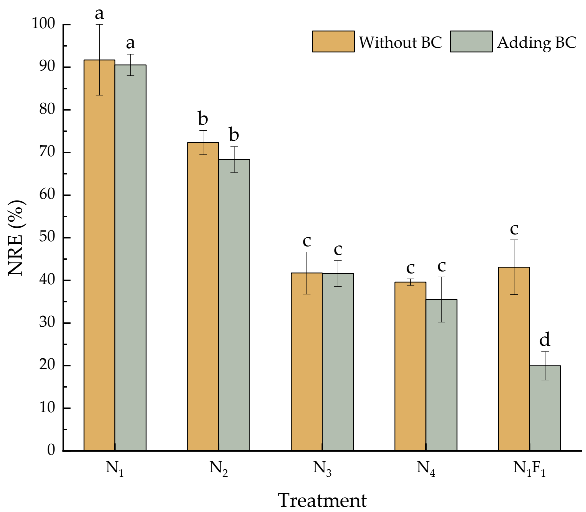

Figure 5. Apparent fertilizer N recovery efficiency (*NRE*). Note: *NRE* in the graph represents means ± standard errors (n = 5). Different letters represent significant differences ($p < 0.05$) in *NRE* for each treatment between different BC allotment levels, urea application amounts, and organic manure amounts. N_0, N_1, N_2, N_3, and N_4 represent the urea application rate, 0, 100, 200, 300, and 400 kg N ha^{-1}, respectively. F_1 represents organic manure of 100 kg N ha^{-1}.

Generally, the fates of urea are usually included three ways including plant recovery, soil retention, and potential loss. The proportion of each component is expressed as ^{15}NRE, ^{15}NRE–$_{soil}$, and ^{15}NLE, respectively (Figure 6). The results of the univariate analysis showed that the amount of urea, BC, and organic manure content significantly affected ^{15}NRE–$_{soil}$. The higher of N application rate was, the higher the ^{15}NRE–$_{soil}$ was. The lowest ^{15}NRE–$_{soil}$ was 2.79% in $N_1B_0F_0$ treatment and the highest ^{15}NRE–$_{soil}$ was 24.79% in $N_4B_0F_0$ treatment. The BC application promoted N enrichment into the soil, averagely increased by 10.76%, 5.95%, 14.49%, and 9.41% at the rates of 100, 200, 300, and 400 kg N ha^{-1}, respectively ($p < 0.05$).

The ^{15}NRE decreased with the increase in N application rate, and plant uptake increased by 77.01% at the 100 kg N ha^{-1} level. Further addition of 100 kg more urea ha^{-1} reduced plant uptake by 4.58% to 17.65% and 12.05% ($p < 0.01$). While the BC application was significant but marginally affected ^{15}NRE. This effect was not singular at different N levels, decreasing by 1.81% and 0.41% at 100 kg N ha^{-1} level and 400 kg N ha^{-1} levels, respectively, while increasing by 1.21% and 0.53% at 200 kg N ha^{-1} and 300 kg N ha^{-1} levels, respectively ($p < 0.01$). In contrast, the mixed urea and organic manure treatments did not have an advantage in promoting plant N uptake, with an average decrease of 30.83% ($p < 0.01$) compared with the only urea treatment at the same total N level. This may be because organic manures are easily lost by decomposition.

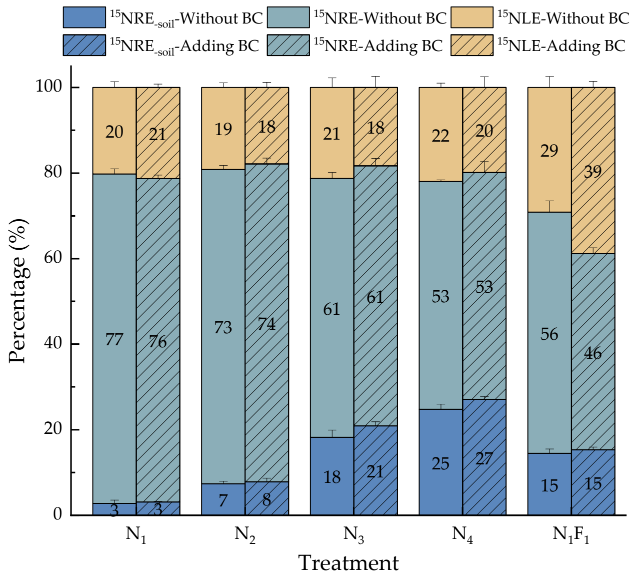

Figure 6. Marking the fate of ^{15}N fertilizer (%). Note: The figure shows the fate of each treatment mark ^{15}N after application to the soil, including being lost, taken up by plants, and retained by the soil. Data are mean ± standard error (n = 5). N_0, N_1, N_2, N_3, and N_4 represent the urea application rate, 0, 100, 200, 300, and 400 kg N ha^{-1}, respectively. F_1 represents organic manure of 100 kg N ha^{-1}.

The potential loss included N leaching and ammonia volatilization, etc. The analysis showed that *^{15}NLE* tended to increase gradually with the increase in urea level. However, the *^{15}NLE* of $N_1B_1F_0$ treatment was higher than that of $N_2B_1F_0$ treatment, which may be because the adsorption of N by BC reduced the distribution of fertilizer to plants at low N level. The potential loss rate for all treatments in this experiment was within 40%, which was attributed to the fine trial management and basically no super field holding leakage during the whole reproductive period. The potential loss rate of treatments with BC addition was reduced by 6.91%, 13.92%, and 9.61% at 200, 300, and 400 kg N ha^{-1} levels, respectively, compared with the conventional treatments ($p > 0.05$). In contrast, *^{15}NLE* was increased by an average of 85.00% ($p < 0.01$) for the treatments with organic manure and urea application with the same total N and was significantly increased by 33.40% in $N_1B_1F_1$treatment compared with $N_1B_1F_0$.

The results showed that 45.84% to 77.01% of the N was absorbed and utilized by the plants after urea was applied to the potting soil. The application of BC, on the one hand, probably enabled the urease inhibitor in BC humic acid [44] and inhibited the hydrolysis of urea in the early stage of pakchoi growth to reduce the loss of N, and as pakchoi growth entered the later stage the water-soluble humic acid in BC was gradually consumed and utilized. After that, the urease inhibition was weakened and gradually dissolved nutrient ions were released into the soils [21]. This process provided sufficient N for pakchoi growth in the vigorous period as a urea retarder. On the other hand, BC as a C source can provide a suitable environment and substrate for ammonifying microorganisms and nitrifying bacteria, which enhances microbial activity and correspondingly increases the inorganic N content of the soil N pool [45]. The absorbed N by BC provided an N source for pakchoi growth. In addition, the drying rate of BC dust was less than the drying rate of the soil, which was beneficial for retaining moisture for a longer period [21], and the dried BC increased soil aeration due to its internal pores. All these provided a good living environment for plant growth and promoted the transition of urea N from the soil to the plant. The experimental results showed that the dosed BC had an inhibitory effect on the uptake of exogenous urea N by the plant at the urea application rates of 100 kg N ha^{-1} and 400 kg N ha^{-1}, while it showed a facilitating effect in the applied N levels of 200 kg N ha^{-1} and 300 kg N ha^{-1}. The reason for this inconsistency may be because the adsorption of nutrients by BC at low N levels reduced the influx of N to the plant, which was similar to the study of using biochar to reduce the ^{15}N recovery of cotton at low N application levels by Wang et al. [31]; after adequately meeting the N requirements of the crop, higher N levels also failed to increase its uptake by the plant but were lost or entered the soil instead. Only the medium N conditions provided a suitable and stable N source for plant growth and development. In addition, we found that although *NRE* and ^{15}NRE were also used to indicate plant uptake of N they did not behave the same way. For example, the treatment with BC addition at the urea application rate of 200 kg N ha^{-1} exhibited lower *NRE* but higher ^{15}NRE values compared to the treatment without the addition of BC. In fact, by splitting the calculation for Equations (1) and (3) *NRE* was determined by the total N uptake of both treatments only, while ^{15}NRE will be influenced by the value of *Ndff* in addition to the total N. For the analysis of pakchoi leaves (Figure 2) and roots (Figure 3), the treatment with BC addition did show higher *Ndff* values at the urea application rate of 200 kg N ha^{-1} level, which suggested that the *NRE* values estimated by isotopic and non–isotopic methods may be different [31]. Regarding N retention, the soil retained after urea was applied to the potting soil, and the amount of N residue increased with the increase in N fertilizer dosage. After pakchoi harvesting the residual ^{15}N content in the soil was higher in the organic–inorganic dosed treatments compared to the inorganic N treatments, and most of the residual fertilizer N was presented in the organic form, which was consistent with the findings of Kumar et al. [46,47]. The dosed application of BC increased soil retention for N ($p < 0.05$), which could be, on the one hand, that BC containing organic C stimulated microbial activity leading to an increase in partial N immobilization in inorganic soil [48], and it has been demonstrated that net N immobilization was mainly microbial to match the high C growth substrate [49]. On the other hand, it may be because the adsorption of NH_4^+ by BC substrates led to N immobilization. Furthermore, BC contains many carboxyl, hydroxyl, and phenolic hydroxyl groups, which can provide many cations exchange sites to retain NH_4^+ synthetic organic matter [44]; the elevated soil retention was a visual representation of the increased inorganic ^{15}N fixation by the application of BC. In addition, the results of the two-factor analysis showed that the interaction between BC and organic manure also had an enhanced effect on soil N retention ($p < 0.01$) but this effect was not significant with organic manure only ($p > 0.05$), which was consistent with the conclusion that the addition of BC to compost increased N retention [50].

After urea was applied to the soil, 17.83–38.86% of the N was lost by leaching or volatilization. It showed a trend that the N loss rate increased with the urea application rate. After pakchoi was harvested, the N loss rate in treatment of $N_1B_1F_0$ slightly increased by 5.45% more than that of $N_1B_0F_0$; the cause maybe because of the N adsorption to BC at low N levels, which was considered the potential loss in the calculation. The rest of the N loss rate at the applied N levels were lower than the treatments without BC application, which can be attributed to the increased immobilization of inorganic N by the application of BC. This was consistent with the finding of Poudel et al. [51], who reported that the application of organic amendments increased the potential of soil to store N and thus reduce N losses.

3.5. Relationship between Indicators

The results of correlations among the indicators of pakchoi using Pearson correlation analysis are shown in Figure 7. Under the conditions of this experiment, pakchoi $^{15}N_{recovery}$ rate was significantly positively correlated with root $^{15}N_{recovery}$, $Ndff\text{–}_{\mathrm{root}}$, $Ndff\text{–}_{\mathrm{leaf}}$, leaf TN uptake, leaf $^{15}N_{recovery}$, leaf NO_3^-;, soil NO_3^-, $^{15}N_{retention}$ and $Ndff\text{–}_{\mathrm{soil}}$ were all significantly positively correlated ($p < 0.01$), and significantly positively correlated with $^{15}NRE\text{–}_{\mathrm{soil}}$ ($p < 0.05$). This showed that crop uptake of inorganic N was closely related to the contribution of fertilizer to the crop and soil, and among the three destinations after fertilizer application the only increase in $^{15}NRE\text{–}_{\mathrm{soil}}$ and ^{15}N uptake of pakchoi were significantly and positively correlated; the increase in soil NO_3^- was a visual representation of the increase in soil N. BC could indirectly promote N uptake by increasing $^{15}NRE\text{–}_{\mathrm{soil}}$.

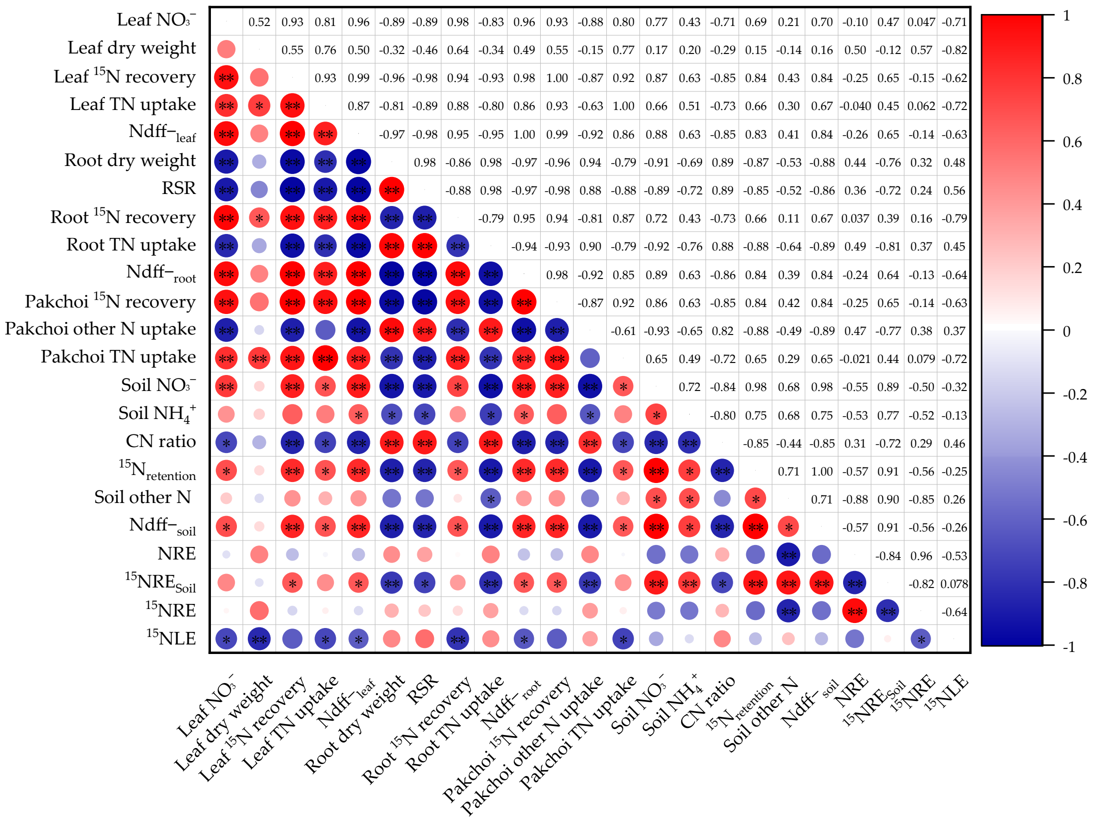

Figure 7. Correlation between the measured indicators. Note: *Ndff* means N derived from fertilizer; RSR means root crown ratio; CN ratio means the ratio of total carbon to total nitrogen in soil; *NRE* means N recovery efficiency; ^{15}NRE means plant ^{15}N recovery efficiency; $^{15}NRE_{soil}$ means soil ^{15}N retention efficiency; ^{15}NLE means potential ^{15}N loss efficiency. The figure shows the correlation between the measured indicators. * and ** indicate a significant correlation at $p < 0.05$ and $p < 0.01$, respectively. The colors and numbers indicate the degree of correlation between the corresponding row comment and column comment, red is a positive correlation, and blue is a negative correlation.

The absorption of N from the soil rather than ^{15}N-labeled urea, on the other hand, showed the opposite of pakchoi $^{15}N_{recovery}$: a significantly positive correlation ($p < 0.01$) with C:N, root TN uptake, RSR, and root dry mass. It was understood that in the case of consistent total N uptake by the crop, external N and the soil native N pool are two sources of supplying nutrients and the dominance of one part of them would lead to lower demand for the other part. These indicators were positively correlated with the absorption of soil native N and were closely related to root development. The higher the C:N was, the more significant the improvement in soil physicochemical properties was [52] and the greater the total N uptake by the root system, thus promoting root growth to improve root mass and the RSR.

Pakchoi TN uptake showed a correlation largely consistent with pakchoi $^{15}N_{recovery}$. Combined with the *Ndff* values in Figures 2 and 3, this could be that more than 50% of the N absorbed by the crop in this experiment after applying more than 200 kg N ha^{-1} came from exogenous urea, and both also showed a significant correlation ($p < 0.01$).

For N utilization and urea N fate, *NRE* values were significantly and positively correlated with, and only with, ^{15}NRE ($p < 0.01$). They increased or decreased simultaneously. However, *NRE* was significantly negatively correlated with $^{15}NRE{-}_{soil}$ ($p < 0.05$). Combined with the results of the one-way ANOVA, these two indicators were only significantly affected by the level of N supply, while an increase in N application led to a decrease in *NRE* and the allocation of exogenous urea to the crop, thereby increasing the proportion of soil retention and N loss.

The $^{15}NRE_{-soil}$ was significantly positively correlated ($p < 0.01$) with $Ndff_{-soil}$, soil other N, $^{15}N_{retention}$, soil NO_3^-, soil NH_4^+, and was significantly positively correlated ($p < 0.05$) with pakchoi $^{15}N_{recovery}$, $Ndff_{-root}$, $Ndff_{-leaf}$. ^{15}NLE was significantly negatively correlated with root $^{15}N_{recovery}$ and leaf dry mass ($p < 0.01$), and with ^{15}NRE, pakchoi TN uptake, $Ndff_{-root}$, $Ndff_{-leaf}$, leaf TN uptake, and leaf NO_3^- ($p < 0.05$). Therefore, in order to reduce ^{15}NLE, the values of leaf NO_3^-, pakchoi TN uptake, leaf TN uptake, and leaf dry mass need to be increased, and according to Figure 2 the addition of BC can increase leaf NO_3^-; or by increasing the percentage of soil retention of fertilizer thereby increasing pakchoi $^{15}N_{recovery}$, etc. This has a direct and indirect positive effect on reducing ^{15}NLE.

3.6. Application Prospect of BC

Overall, the results suggested that the combined application of BC with N fertilizer was beneficial for vegetable production. This was directly supported by the $^{15}NRE_{-soil}$ and ^{15}NRE. The mechanism of increasing fertilization benefits maybe because that BC application increased soil organic matter, provided suitable environment and substrate for ammoniating microorganisms and nitrifying bacteria, enhancing microbial activity. However, since the single crop season BC application had no significant influence on soil C:N, the key reason was the unique physical and chemical properties of BC. The demand for nutrients in the early stage of crop growth was less, and urease inhibitors in BC humic acid reduced the hydrolysis of urea in the early stage. BC had many ions exchange groups capable of complexation or adsorption, and strong physical adsorption, which increased the ability of soil to store nutrients and reduced N leaching. In addition, the porous structure of BC results in higher water retention and soil permeability, providing a good rhizosphere environment for plant growth. The yield increase effect of BC was not significant in the single-season trial, which may be because the BC material in the experiment was only physically dried and pulverized, but not chemically activated and modified, so the potential of BC could not be better unleashed.

The BC is unsuitable for combustion, but its unique properties can immobilize pollutants and make nutrients and trace elements more accessible to plants. Due to stable structure BC can remain in the soil for 100–1000 years [53], increasing organic C for a long time [54]. Currently, the BC resources are abundant all over the world. Being in the early stages of coalification, the nature of BC can vary greatly depending on the origin and quality. However, Victoria has abundant and cheap BC resources, and BC's ash and heavy metal content were low [55]. In this single-season trial, BC has a good effect on the distribution of exogenous N in the plant–soil system, increasing soil retention and reducing N losses. Since there was a lack of research on the application of BC in agricultural soils and mainly short-term trials, it was important to evaluate the changes in soil quality due to the long-term application of BC, and the focus of research on the use of BC should also be on activation and modification to make it a better nutrient carrier for long-term experiments [56]. Due to its low price, it has a clear advantage over traditional biochar. BC may have a promising application in agriculture as a fertilizer loss retarder or soil amendment if the optimal dosage combination is determined under the local conditions.

4. Conclusions

Application of BC significantly affects the fate of exogenous N in the soil–plant system. BC can reduce N loss in the environment by increasing the N retention in the soil and the distribution of fertilizer N in the plant, ensuring that plants can obtain N fertilizer for a longer period, and indirectly improve the utilization efficiency of fertilizer. Moreover, this effect became significant with the increase in N application rate, highlighting the important role of BC in N retention. This work provides a proof of concept for the use of BC. The results showed that 200 kg N ha^{-1} fertilizer combined with 5 t ha^{-1} BC could maintain a high *NRE* and pakchoi yield. However, further work is needed to verify the results of the BC application in field conditions.

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