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Effects of rice cropping intensity on soil nitrogen mineralization rate and potential in buried ancient paddy soils from the Neolithic Age in China's Yangtze River Delta

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Abstract
Purpose Rice cropping density, rice cropping duration, and fertilization can affect soil nitrogen (N) supply, but rice cropping intensity (RCI) on soil N fertility is not fully understood, particularly for ancient paddy soils without N fertilization.
Materials and methods Eight buried ancient paddy soils from the Neolithic Age in China's Yangtze River Delta, and its parent material, and seven present paddy soils in the same fields were used to investigate the effects of RCI on soil nitrogen mineralization rate and potential. In the present study, concentration of phytolith of rice in soils was used to indicate the RCI.
Results and discussion Soil N content was obviously greater in the buried Neolithic paddy soils than in the parent material. Total soil N increased with increasing phytolith from 5,200 to 60,000 pellets g^{-1}, but tended to decrease with increasing phytolith from 60,000 to 105,000 pellets g^{-1}. A possible reason for RCI-induced increase of soil N was due to biological N_2 fixation in the rice field because there was a significant negative relationship between total N and $\delta^{15}N$ in the buried Neolithic soils. The mineralization rate constant (k) ranged from 0.0126 to 0.0485 d^{-1} with an average of 0.0276 d^{-1}, which was similar to that of the parent material, but lower than those in the present paddy soils. The *k* value increased with increasing RCI in the Neolithic paddy soils. There was a significant positive relation between RCI and the percentage of cumulative mineralizable N in the 14 d of that within 103 d incubation.
Conclusions Soil N content tended to increase with the increasing intensity of rice cropping and then decreased under the high intensity of rice cropping; the excessive high intensification of rice cropping could facilitate fast N mineralization (labile N) fraction in the cumulated mineralized N. The unfertilized paddy field could only meet soil N supply under the low intensification of cropping rice in the Neolithic Age. The N fertilization is necessary in order to improve soil fertility for sustaining the present high-yield rice production.

Keywords ^{15}N natural abundance · Ancient soil · Nitrogen mineralization · Rice cropping intensity · Rice phytolith · Soil fertility

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1 Introduction

Rice is an important main food crop in the world, particularly for Asia. More than 50% of the world's population feeds on it. China has a long history for cultivating rice, which can be traced back to 7,500–8,500 years BP (Greenland 1997; Ding 2004; Cao et al. 2006). Currently, the area of rice paddy field in China is about 29.3 million ha, which represents about 19% of the total world rice paddy field area and yields around 30% of the total world rice grain (FAOSTAT 2005).

Soil organic C (SOC) and total N (TN) contents play a crucial role in sustaining agricultural production systems. About 95% of soil total N is in the organic form and only a small fraction of this is mineralized into the plant available forms by microbial processes during a plant growing season (Li 1992; Burton et al. 2007; Pan et al. 2008; Xu et al. 2008). The availability of soil organic N is affected by various environmental factors and management practices (Xu et al. 1993, 1996; Chen et al. 2002; Blumfield et al. 2005), including growing plants (Li 1992; Zhu and Wen 1992; Chen and Xu 2006; Xu et al. 2009). The influence of growing rice on N mineralization and availability in the present paddy soils has been studied previously (Cai and Zhu 1983; Kundu and Ladha 1997; Saito et al. 2006; Roder et al. 1995; Funakawa et al. 1997). Some studies recorded more mineral N in the flooded soil planted with rice than in the unplanted soils (Cai and Zhu 1983). Mineral N availability was significantly higher in the planted rice soils than in the unplanted soils (Kundu and Ladha 1997).The increasing cropping intensity (the frequency of planted rice crops without irrigation during a given period of time) reduced the soil N availability (Saito et al. 2006). Total C content and N availability decreased as the fallow period declined (Roder et al. 1995; Funakawa et al. 1997). All of these experiments were designed to study N availability/mineralization in the present paddy soils treated with fertilizer N. The difference of N supply levels could affect cropping-induced change of soil N availability / mineralization. Unfortunately, few present paddy fields are not fertilized since 1950s. Little information is available regarding the influence of rice cropping on N availability in the ancient paddy soils without fertilization practice. Our study used a few rare, valid Neolithic paddy fields to examine the influence of rice cropping intensity (RCI) on N supplying potential of unfertilized paddy soils from the Neolithic Age in China's Yangtze River Delta. These results might provide useful information not only for investigations of maintaining mechanism for the ancient paddy soil fertility, but also for the evaluation of sustainability in the present paddy soils.

2 Materials and methods

2.1 Study site description

The soils used in this study were taken from Chuodun site (31° 24′ 07″N and 120° 50′ 41″E), in the lower reaches of Yangtze River, China. The Chuodun site has a history of cultivating rice for more than 6,000 years in which a complete irrigation system was found (Cao et al. 2006). During the period from 1978 to 2003, six excavations were performed by the archeologists and soil scientists (Gu 2003; Suzhou Museum 2003; Cao et al. 2006). In the fifth excavation, 24 fields were dug and their ages could be traced back to Majiabang Culture period (Neolithic Age) (around 6,000 a BP) (Gu 2003). The sixth excavation had an area with about 300 m^2 and 22 ancient paddy soil fields were observed in the buried layer called as Majiabang culture layer where they were located about 1 m from the field surface (Gu 2003). The boundary of each rice field was confirmed by the carbonized rice, distribution of ridges and ditches as well as the contents of plant phytoliths (Gu 2003; Cao et al. 2006).

2.2 Definition of rice cropping intensity

It is well known that cropping intensity is linked to the rice-growing duration, and planting density for rice. Unfortunately, these parameters for the ancient rice planting were not recorded. Phytoliths, also called opal phytolith, plant opal, or grass opal, are plant-derived silica body ($SiO_2 \cdot nH_2O$), whose shape and size are physiologically and chemically stable, remaining in the soil for more than 10,000 years under good conditions (Hiroshi 1976; Fujiwara 1993; Zhao 1998). Phytoliths occur in stems, leaves, roots, and inflorescences of plants. Phytoliths or plant opals, the motor cell phytolith of rice, have been used to indicate the presence of domesticated rice in archeological site (Fujiwara 1993; Zhao 1998); to estimate rice yield in the ancient paddy fields (Fujiwara 1993); and to distinguish the two main subspecies of rice (*indica and japonica*) (Wang et al. 1996) according to morphological traits of phytolith of rice; and to be a typical evidence to reflect the intensity of cultivating rice in ancient times (Hiroshi 1976). It could be reasonably speculated that the more rice phytolith in the soil, implying the longer and/or thicker for planting rice plant at the investigation sites at the Neolithic Age. We define an intensity of cropping rice as below for evaluation of cropping rice on nutrients change, and nitrogen mineralization in the paddy soils:

- Absolute intensity of rice cropping (RCI) = Absolute quantity of rice motor cell phytolith per gram soil

- Relative intensity of rice cropping (RRCI; %) = ×100 (Motor cell phytolith of rice in the soil)/(phytolith of plants in the soil)

2.3 Soil sampling

The archeological excavation was described in the standard procedures of China's Archaeological Society (Suzhou Museum 2003). The digging, recording, description, and analysis of soils were determined by the conventional methods stated by the Society of Soil Science of China (SSSC; 2000). Soil samples were taken from 15-cm soil depth between the center of the buried layer in each field for analyzing plant phytoliths. The samples were air-dried and passed through a 2-mm sieve for the analysis of soil fertility parameters.

The soils with >5,000 rice pellets phytoliths per gram soil were defined as rice cultivated paddy soils (Hiroshi 1976). In the present study, the eight buried prehistoric Neolithic paddy soils with rice phytoliths more than 5,000 pellets per gram soil (NL-1–NL-8, in which NL is the abbreviation of the "Neolithic Age") and a total of seven surface present paddy soils taken from the same fields with similar area to eight buried prehistoric rice paddy fields (PP-1–PP-7, in which PP is the abbreviation of "present paddy soil"), as well as the parent material for prehistoric Neolithic paddy soils (PM, in which PM is the abbreviation of the "parent material") were used to compare soil pH, soil organic C (SOC), total nitrogen (TN), NH_4-N, NO_3-N, and phytoliths. A total of four buried prehistoric Neolithic paddy soils with a series of rice phytoliths (5,205, 13,871, 29,723, and 105,159 pellets g^{-1} soil), and PM (0 pellets g^{-1} soil), PP-1 (19,476 pellets g^{-1} soil) were used to investigate the N mineralization characteristics of the soils.

2.4 Chemical analysis

The evolved times of ancient paddy soils were judged by the layers where they would lie and ancient cultured rice was buried there. The age of ancient paddy fields was determined by ^{14}C dating in the organic matter and in carbonized rice (Qiu 1990; Cao et al. 2006). Plant phytolith in the soil was determined by glass particle method (Hiroshi 1976; Wang et al. 1996). The soil phytolith contents were listed in Table 1. The soil pH was measured in a mixture with the 1 M KCl (1:2.5, *w*/*v*), using a glass electrode (HANNA-PH211A). Soil organic carbon was analyzed by the oxidation of potassium dichromate ($K_2Cr_2O_7$). Soil total N was measured using the Kjeldahl method. Soil NO_3^--N and NH_4^+-N were extracted by 2 M KCl solution (1/10, *w*/*v*), NO_3^--N was determined by dual-wavelength (220 nm and 275 nm) spectrophotometry method, and NH_4^+-N was determined by indophenol blue photometric method (SSSC 2000). Basic properties of the buried Neolithic paddy soils were presented in Table 2. ^{15}N natural abundance in the soils was determined after Semimicro-Kjeldahl digestion on a Finnigan-MAT 251 Mass Spectrometer (Boutton and Yamasaki 1996).

2.5 Incubation experiments for N mineralization

The ancient paddy soils were lack of an initial trigger of active microorganisms (Hu et al. 2005). Microorganism inoculation was used to ensure to have enough active microorganisms. The 4 g for each soil sample was transferred to a plastic bottle with 200 ml distilled water, and then the plastic bottle was shaken for 1 h, whereafter placed for 4 h. The clear solution was transferred to 250 ml plastic bottle as microorganism inoculation solution for the incubation experiment.

Table 1 Plant phytolith (pellet g^{-1} soil) in buried Neolithic paddy soils, parent material, and present paddy soil taken at Chuodun site in China's Yangtze River Delta

	Sample number	Rice (Oryza)	Phragmites	Miscanthus	Bambusoidear	Panicum	Total phytolith[a]	Percentage (%)[a]
Neolithic	NL-1	5,205	0	7,286	0	0	12,491	41.7
	NL-2	5,838	0	11,677	0	973	18,488	31.6
	NL-3	6,503	4,335	15,174	0	0	26,012	25.0
	NL-4	12,773	2,737	12,773	0	0	28,283	45.2
	NL-5	13,804	3,681	29,449	0	0	46,934	29.4
	NL-6	13,871	1,982	11,889	0	991	28,733	48.3
	NL-7	29,723	2,972	5,945	0	1,982	40,622	73.2
	NL-8	105,159	0	6,632	0	0	111,790	94.1
Present	PP-1	19,476	1,025	15,376	7,175	3,075	46,127	42.2
Parent material	PM	0	0	1,009	0	0	1,009	–

NL Neolithic Age paddy soil, *PP* present paddy soil, *PM* parent material

[a] Total phytolith stands for absolute intensity of rice cropping (RCI) and percentage of rice opals in total plant phytolith opals stands for relative intensity of cropping rice (RRCI)

Table 2 Basic properties of buried Neolithic paddy soils, parent material, and present paddy soils taken at Chuodun site in China's Yangtze River Delta

	Sample number	pH	SOC (g kg^{-1})	TN (g kg^{-1})	NO_3-N (mg kg^{-1})	NH_4^+-N (mg kg^{-1})
Neolithic	NL-1	5.46	6.06	0.54	0.71	0.59
	NL-2	5.54	6.88	0.55	0.76	0.94
	NL-3	5.37	6.92	0.64	2.21	2.40
	NL-4	5.92	17.31	1.17	1.47	2.41
	NL-5	5.60	11.58	0.81	0.71	0.00
	NL-6	5.96	6.21	0.60	0.70	0.77
	NL-7	6.01	16.00	1.11	0.67	2.24
	NL-8	5.85	12.88	1.02	1.69	1.99
	Mean (n=8)	5.71	10.48	0.80	1.12	1.42
	CV (%)	4.38	43.80	32.50	52.68	66.90
Present	PP-1	5.24	13.06	1.25	6.71	0.19
	PP-2	4.94	13.58	1.47		
	PP-3	4.72	25.10	2.53		
	PP-4	4.79	24.46	2.63		
	PP-5	4.34	24.72	2.65		
	PP-6	4.69	24.18	2.65		
	PP-7	4.77	25.73	2.78		
	Mean	4.78	21.55	2.28		
	CV (%)	5.68	26.19	27.89		
Parent material	PM	6.12	4.00	0.30	0.44	4.95

SOC soil organic C, *TN* total N

An aerobic incubation with intermittent leaching procedure followed that of Stanford and Smith (1972) using quadruplicate soil samples was used to evaluate the soil N mineralization potential. For each soil, 15 g soil was mixed with 15 g of acid-washed quartz, and 2-ml microorganism inoculation solution in a 100-ml plastic beaker, subsequently transferred to 100-ml plastic incubation tube. A fiberglass was placed below and on top of the soil–sand mixture. The top filter protected the soil sample from disaggregation and slaking during leaching (MacKay and Carefoot 1981; Bonde and Rosswall 1987).

Before incubation, the soil–sand mixture was leached using 100 ml 100 mM $CaCl_2$ in 25 ml increments, followed by 25 ml of minus-N nutrient solution (i.e., 0.002 M $CaSO_4$, 0.002 M $MgSO_4$, 0.005 M $Ca(H_2PO_4)_2$, and 0.0025 M K_2SO_4). After leaching was completed, a vacuum (60 cm Hg) was applied to adjust the moisture content of the samples (Stanford and Smith 1972). The soil column was incubated at 35°C and leached at the 7, 14, 28, 42, 58, 73, 103 days after the incubation using the same procedure as for the pre-incubation leaching described as above. The leachates were collected in 250-ml flasks and brought to volume (250 ml). During incubation, the tubes were covered by plastic film for retarding moisture loss, and aerated once every day. Part of this solution was transferred to a 60-ml plastic bottle and refrigerated. Leachates were analyzed for NO_3^--N (dual-wavelength spectrophotometry method), and NH_4^+-N (indophenol blue photometric method) as described by SSSC (2000). Total mineral-N was calculated by summing the amounts of NH_4^+-N and NO_3^--N.

2.6 Mineralization model

Soil N mineralization has commonly been described by a first order model (Juma et al. 1984; Ellert and Bettany 1988):

$$N_t = N_0\left(1 - e^{-kt}\right) \quad (1)$$

where N_t is the cumulative net N mineralized up to time t (d); k is the rate constant (d^{-1}); and N_0 is defined as the potentially mineralizable N pool at time 0.

The first derivative of Eq. 1 is

$$dN_t/dt = (N_0 \times k)e^{-kt} \quad (2)$$

The first derivative shows that the rate of N mineralization decreases with time and that it is a function of N_0 and k.

2.7 Statistics analysis

SigmaPlot 10.0 software was used to fit curves between incubation time (t) and mineralized N. The chemical and modeling data were analyzed using the SPSS 10.0 (SPSS

Inc., Standard Version). Analysis of variance for chemical data were undertaken, and nonlinear regression was used to fit mineralization data to the first order model for estimating N mineralization dynamic parameters.

3 Results and discussion

3.1 Fertility characteristics of buried Neolithic paddy soils

The pH values of eight ancient paddy soils were 5.37–6.01 with a mean value of 5.71. The average pH value in the seven recent paddy soils taken in the same fields was 4.78, which was lower than that of the ancient paddy soils ($p<0.001$), pH value in both ancient and present paddy soils were also lower than that of the parent material (see Table 2). The reason for this might result from atmospheric acid precipitation and intensive application of chemical N fertilizers. The rate of atmospheric sulfur precipitation and the frequency of acid rain in Yantze River Delta were high (Wang et al. 2005).

The contents of soil organic C in the eight buried ancient paddy soils ranged from 6.06 to 17.31 g kg^{-1} with a mean of 10.48 g kg^{-1} and were 2.6-folds of that in parent material (see Table 2). It is obvious that soil organic C increased after parent material evolved into the paddy soils at Chuodun Site in China's Yangtze River in the Neolithlic period. The contents of organic C in the buried ancient paddy soils were 51.4% lower than those of the present paddy soils (see Table 2).The average contents of organic C in 471 recent soils in Taihu lake region were 14.9 g kg^{-1} (Xu et al. 1980). The contents of organic C in 59 recent paddy soils in Wuzhong district in Suzhou City were almost the same as in Chuodun Site, which were 13.2 g kg^{-1} (Cao et al. 2002). It could be concluded that the contents of organic C in the recent paddy soils were greater than those in the buried ancient paddy soils.

The contents of total N in the eight buried ancient paddy soils ranged from 0.54 to 1.17 g kg^{-1} with a mean value of 0.80 g kg^{-1}, which was markedly higher than that in the parent material, but was obviously lower than those in the present paddy soils (see Table 2). Soil total N increased after the parent material was evolved into the paddy soils at Chuodun site in China's Yangtze River in the Neolithic period. The pollen analysis of the parent material revealed that the dominant plants in the parent materials were not aquatic species, but woody and herbaceous plants (Li et al. 2007). The pollen analysis of the parent material combined with the color reveal that the parent material could be originated from the wind-driven deposition loess. The loess has a lower content of organic N and C (Gu 2003). Therefore, loess which is distributed in China's West region could evolve into the higher N fertility paddy field if the region has enough water resources because the present results indicated soil N increased after loess was evolved into the paddy fields in the Neolithic period. The mean contents of total N in 458 paddy soils in Taihu lake region was 1.49 g kg^{-1} (Xu et al. 1980), which was much greater than that in the buried ancient paddy soils.

Coefficients of variation (CV) of organic C and total N in the ancient paddy soils from the eight buried prehistoric Neolithic paddy fields were higher than those of the present paddy soils from the same area fields (see Table 2), which suggests that the variation of organic C and total N contents in the soils decreased with the increase of human activities. The agricultural practices in the Neolithic period were extensive cultivation compared with those in the present period. The present cultivation practice could be a major reason resulting in uniformity of soil fertility.

Soil total N increased with increasing rice phytolith from 5,200 to 60,000 pellets g^{-1}, but decreased with the increasing rice phytolith from 60,000 to 105,000 pellets g^{-1}. Soil total N and soil organic C increased with the increase of rice cropping intensity, subsequently decreased with the increasing of rice cropping intensity (Fig. 1). There was an obvious quadratic function relation between soil total N/soil organic C and the rice cropping intensity in the Neolithic paddy soils (see Fig. 1). The reasons for cropping rice-induced increase of soil total N/soil organic C could be explained as follow. Firstly, the excretion of organic matter of variable C and N contents from growing rice plants, together with sloughing and dying back of roots, could result in the addition of a large amount of decomposable organic materials to the soils. Secondly, some N_2 fixation in flooded soils was found to be associated with rice roots (Rinaudo and Dommergues 1971; Yoshida and Ancajas 1971). Root-associated N_2 fixation in the wetland rice has been estimated at 1 to 7 kg N ha^{-1} per crop season (Roger and Ladha 1990). Thirdly, N_2 fixation by blue algae exists in the paddy soils (Xu et al. 1980; Xiong and Li 1990). There was a significant, negative relationship between $\delta^{15}N$ and total N in the buried Neolithic paddy soils at Chuodun site in China's Yangtze River (Fig. 2). The $\delta^{15}N$ is 0 for atmospheric N_2, and −6‰ to 16‰ for soil N (Mariotti 1983; Shearer et al. 1978). Soil N derived from atmospheric N_2 should result in soil $\delta^{15}N > -6$‰, also <16‰. The present results demonstrated that the $\delta^{15}N$ for the buried Neolithic paddy soils ranged 8‰ to 14‰.Therefore, the paddy soil N would be originated from the atmospheric N_2. The N in the ancient paddy soils is likely to result from mainly non-symbiotic N_2 fixation. The excessive rice cropping intensity resulted in the decrease of soil total N and soil organic C (see Fig. 1). This could be attributed to the burning straw as the field practice in the Neolithic period. The solid state ^{13}C NMR spectra of the fossil rice grains and the SOM in the uppermost layer of the

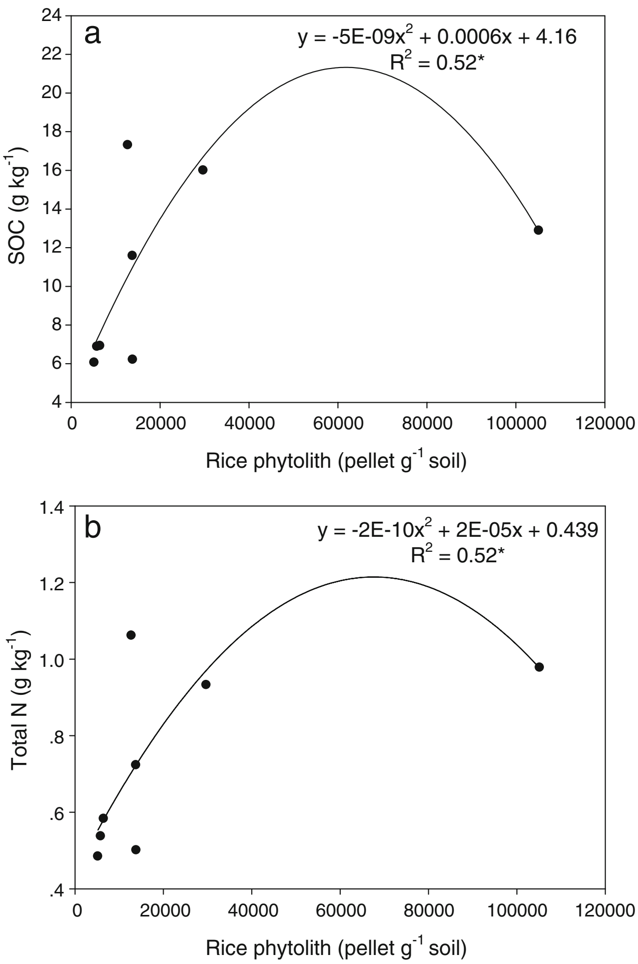

Fig. 1 Relationship between rice phytolith and soil organic C (*SOC*) (**a**) or total N (**b**) in the buried Neolithic paddy soils at Chuodun site in China's Yangtze River ($R_{0.01,\ 8}{}^2$=0.64; $R^2{}_{0.05,\ 8}$=0.44)

prehistoric irrigated rice field assign most of their C as derived from charred rice residues having remained in the ash after postharvest burning (Cao et al. 2006). The practice of "to plow with fire and to weed with water" represents an important aspect of early irrigated rice cultivation in the study fields (Gu 1998; Cao et al. 2006). When the uptake of N in rice was more than the nonsymbiotic N_2 fixation, burning straw would result in loss of N from the soil–rice system. Therefore, it could be concluded that the moderate intensity of rice cropping could maintain soil fertility. Excessive high intensification of rice cropping could result in the decreasing of soil fertility, particularly with low rate straw return to the fields.

3.2 Net nitrogen mineralization

The total net mineral N accumulated within the 103 days ranged from 7.15 mg kg^{-1} to 15.70 mg kg^{-1} with a mean value of 10.80 mg kg^{-1}, which was a little bit higher than that in the parent material (10.39 mg kg^{-1}), but lower than that in the present paddy soil (88.83 mg kg^{-1}; Table 3). The cumulated mineralized N for the first 14 days (fast mineralization fraction) ranged from 2.44 mg kg^{-1} to 7.18 mg kg^{-1} with a mean value of 4.67 mg kg^{-1}, which was a little bit higher than that in the parent material, but lower than that in the present paddy soil (see Table 3). Percentage of cumulated mineralized N for the first 14 days (N_{14}) in that for 103 days (N_t) ranged from 30.2% to 58.5% with a mean value of 42.1%, which was similar to that in the parent material, but lower than that in the present paddy soil (see Table 3). There were significant, positive relationships between N_{14}/N_t and RCI (R^2=0.94, P<0.01), and between N_{14}/N_t and relative rice cropping intensity (RRCI; R^2=0.85, P<0.05; Fig. 3). High intensification of rice cropping resulted in the increasing of fast N mineralization fraction in cumulated mineralized N for the first 103 days.

3.3 Kinetic description of N mineralization

The net mineral N accumulation curves for the study soils resembled a first order kinetic response (R^2=0.94–0.97, P< 0.01; Fig. 4). The N_0 estimated for the buried Neolithic paddy soils, using a first-order model, ranged from 7.3 mg kg^{-1} to 16.9 mg kg^{-1} with a mean value of 11.7 mg kg^{-1} which was a little bit higher than that in the parent material, but obviously lower than that in the present paddy soil (see Table 3). The average N_0 estimated for the six recent paddy soils taken in Taihu lake region, using a first-order model, ranged from 83 mg kg^{-1} to 222 mg kg^{-1} with a mean value of 126 mg kg^{-1} (Li et al. 2003). It could be concluded that the potentially mineralizable N pool (N_0) was obviously lower in the buried Neolithic paddy soils than in the present paddy soils in China's Yangtze River

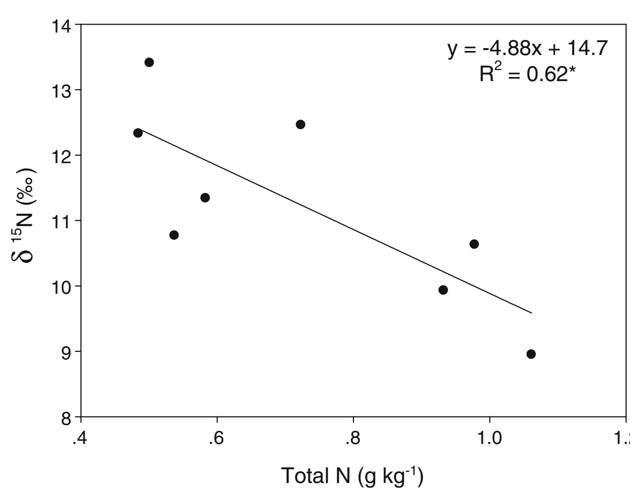

Fig. 2 Relationship between ^{15}N natural abundance (δ^{15}N) and total N in the buried Neolithic paddy soils at Chuodun site in China's Yangtze River ($R_{0.01,\ 8}{}^2$=0.64; $R_{0.05,\ 8}{}^2$=0.44)

Table 3 Comparison of nitrogen (N) mineralization dynamic parameters in the buried Neolithic paddy soils, parent material, and present paddy soil at Chuodun site in China's Yangtze River Delta

	Sample number	N_0[a] (mg kg^{-1})	k[b] (d^{-1})	R^2	N_{14}[c] (mg kg)$^{-1}$	N_{14}/N_0 (%)	N_t[d]	N_{14}/N_t (%)
Neolithic	NL-1	11.45	0.0126	0.95	2.44	21.31	8.08	30.20
	NL-6	16.89	0.0237	0.97	6.16	36.45	15.70	39.24
	NL-7	7.27	0.0254	0.94	2.88	39.62	7.15	40.28
	NL-8	11.32	0.0485	0.95	7.18	63.46	12.27	58.52
	Mean	11.73	0.0276	0.95	4.67	40.21	10.80	42.06
Present	PP-1	86.88	0.0595	0.97	58.04	66.8	88.83	65.3
Parent material	PM	10.37	0.0276	0.97	4.37	42.1	10.39	42.1

[a] Potentially mineralable N

[b] N mineralization rate constant

[c] Cumulated mineralized N for the first 14 days

[d] Cumulated mineralized N for 103 days

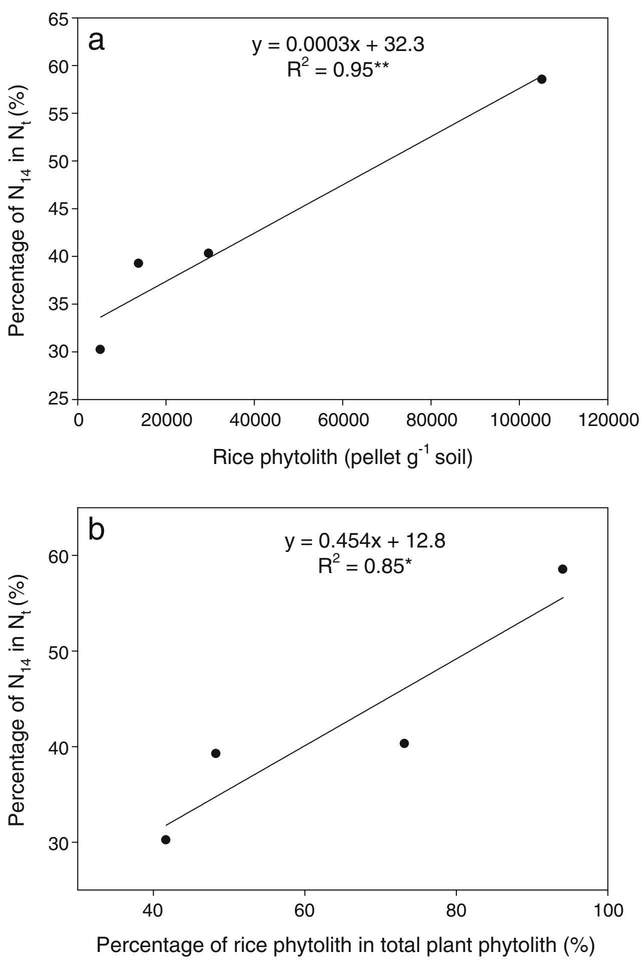

Fig. 3 Relationship between percentage of N_{14} in N_t and rice phytolith (**a**) or percentage of rice phytolith in total plant phytolith (**b**) in the buried Neolithic paddy soils at Chuodun site in China's Yangtze River ($R_{0.01,\ 4}{}^2$=0.92; $R_{0.05,\ 4}{}^2$=0.77)

Delta. Percentage of N_{14} in N_0 ranged from 21.3% to 63.5% with a mean value of 40.2%, which was a little bit lower than that in the parent material, but lower than that in the present paddy soil (see Table 3).

There were significant, positive relationships between N_{14}/N_0 and RCI (R^2=0.92, P<0.05), and between N_{14}/N_0 and RRCI (R^2=0.87, P<0.05; Fig. 5). High intensification of rice cropping resulted in the increasing of fast N mineralization fraction in the potential mineralizable N.

The rate constant ranged from 0.0126 to 0.0485 d^{-1} with a mean value of 0.0276 d^{-1}, which was similar to that in the parent material, but was lower than that in the present paddy soil (see Table 3). The average k estimated for the six recent paddy soils taking in Taihu lake region, using a first-order model, ranged from 0.04 d^{-1} to 0.13 d^{-1} with a mean value of 0.08 d^{-1} (Li et al. 2003). High intensification of rice cropping resulted in the increase of mineralizable N. It could be concluded that the rate constant was obviously lower in the buried Neolithic paddy soils than in the present paddy soils in China's Yangtze River Delta.

There were significant positive relationships between k and RCI (y=3E-07x+0.0152, R^2=0.95, P<0.01), and between k and RRCI (y=0.0006x−0.0097, R^2=0.85, P< 0.05; Fig. 6). As mentioned earlier, the N in the buried Neolithic paddy soils could be originated from the root-associated N fixation. Ito and Watanable (1981) confirmed that the biologically fixed N would mineralize faster than the native soils N and become available to the rice plants.

3.4 Comparison of N supply capacity and intensity between the present paddy and the buried Neolithic paddy soil

High-quality soil possesses the characteristic with large N supply capacity and high N supply intensity. Soil N content is an index for soil N supply capacity, and the potentially

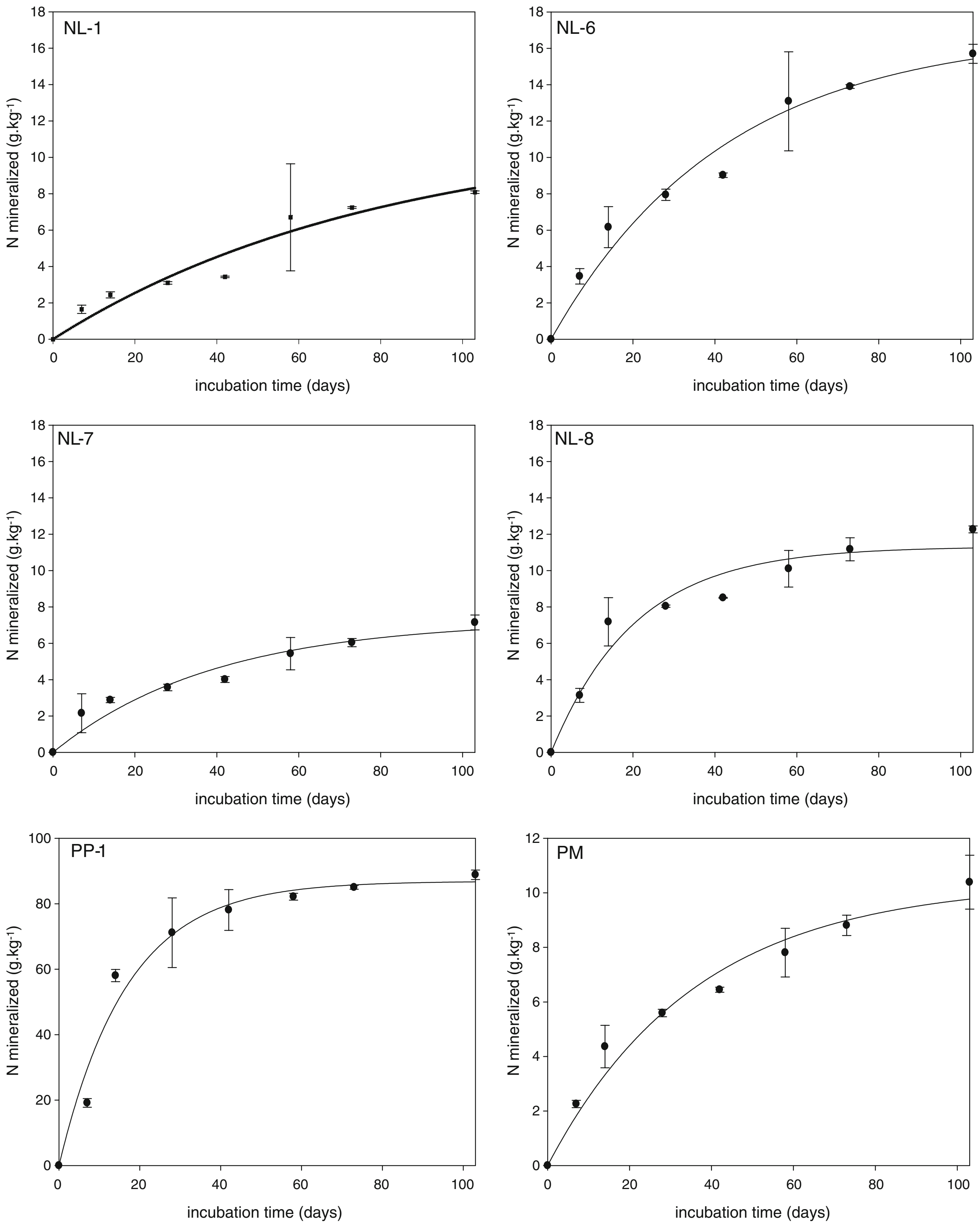

Fig. 4 Cumulative N mineralization in the buried Neolithic paddy soils (*NL-1*, *NL-6*, *NL-7*, and *NL-8*), present paddy soil (*PP-1*), and parent material (*PM*) at Chuodun site in China's Yangtze River Delta

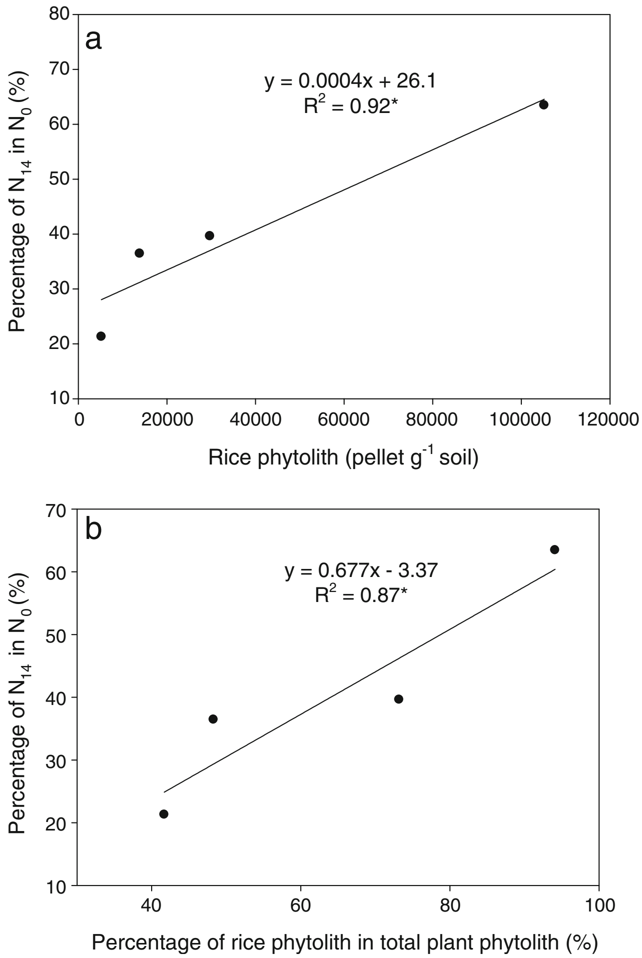

Fig. 5 Relationship between percentage of N_{14} in N_0 and rice phytolith content (**a**) or percentage of rice phytolith in total phytolith (**b**) in the buried Neolithic paddy soils at Chuodun site in China's Yangtze River ($R_{0.01,\ 4}{}^2$=0.92; $R_{0.05,\ 4}{}^2$=0.77)

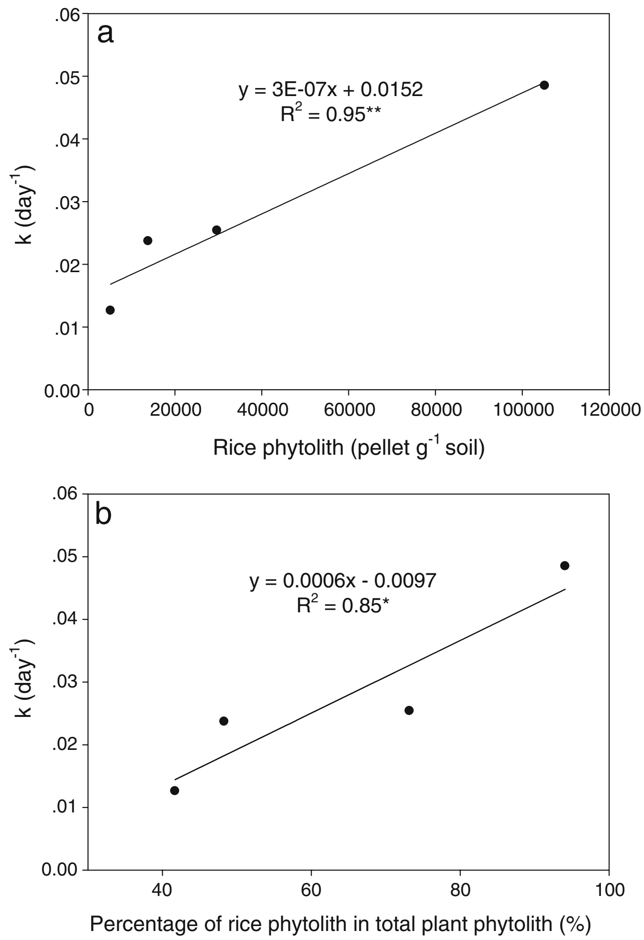

Fig. 6 Correlation of N mineralization rate (k) constant and rice phytolith content (**a**) or percentage of rice phytolith in total phytolith (**b**) in the buried Neolithic paddy soils at Chuodun site in China's Yangtze River ($R_{0.01,\ 4}{}^2$=0.92; $R_{0.05,\ 4}{}^2$=0.77)

mineralizable N pool (N_0) and fast N mineralization were used to evaluate soil N supply intensity (Zhu and Wen 1992). The present results demonstrated that soil organic C, soil total N, N_0, k, N_{14}/N_0 were obviously lower in the buried Neolithic paddy soils than in the present paddy soils taken in the same fields (see Tables 2 and 3), implying that the present paddy soil possesses large N supply capacity and intensity compared with the buried Neolithic paddy soil. This difference of N supply capacity between the buried Neolithic paddy soils and the present paddy soils could be mainly attributed to the difference of rice straw biomass and rice straw returned to the field, and fertilization. According to the conditions at that time, the straws were not returned into the fields directly but were burned at the Neolithic period (Cao et al. 2006). However, rice straws were partly returned into the fields directly in the present agricultural practice. Rice biomass was several-folds higher in the present than in the ancient age. Rice yields were 0.34 t ha^{-1} before 206 BC, which were lower than those in 1956–1965 (2.50 t ha^{-1}), and in 1991–1993 (5.80 t ha^{-1}) (Greenland 1997; Wu 1985). Another reason could be due to the heavy application of chemical and organic fertilizers in the present agricultural practice.

The difference of N supply intensity between the buried Neolithic paddy soils and the present paddy soils could be explained as follow. Firstly, there is difference of the aging of organic N in the soils because the decomposition of soil organic N (SON) over thousands of years could also lower the potentially mineralizable N pool (N_0) and fast N mineralization (labile N) fractions in the cumulated mineralized N in the Neolithic ancient paddy soils, and the buried paddy soils could be those of aged SON fractions. Secondly, the soil N pool difference could be caused by the fertilization and rice straw return between the Neolithic period and the present age. Thirdly, there is the difference of microbial biomass between the buried Neolithic paddy soils and the present paddy soils, though the tested soils were done using microorganism inoculation. The present paddy soils could have an obvious higher microbial activity than those induced by the inoculation in the ancient paddy soils (Hu et al. 2005).

4 Conclusions

Soil total N content was greater in the Neolithic paddy soils than in the parent material, implying that soil organic N increased after loess parent material was evolved into the paddy soils at Chuodun Site in China's Yangtze River in the Neolithic period. Soil N content tended to increase with the increasing intensity of rice cropping, and then decreased under the high intensity of rice cropping. N mineralization rates increased with the increasing intensity of rice cropping in the Neolithic paddy soils. It could be concluded that the high intensification of rice cropping could decrease soil total N, but increase fast N mineralization (labile N) fraction in cumulated mineralized N. The unfertilized paddy field could only meet soil N supply at the low intensification of cropping rice in the Neolithic Age. The N fertilization is necessary in order to maintain soil fertility to meet the present high-yield rice production.

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