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# Influence of water management on the mobility and fate of copper in rice field soil

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**Abstract**

*Purpose* With widely applied water-saving irrigation techniques, the transformation and availabilities of copper (Cu) as both a micronutrient and a toxic metal are changed. However, little information is available on the binding forms, bioavailability, and fate of Cu in paddy fields with different irrigation management. Thus, we investigated the effects of irrigation management on the binding forms and the fate of Cu in a non-polluted paddy soil.

*Materials and methods* Field experiments were conducted in 2011 on non-polluted rice fields in Kunshan, East China. Non-flooding controlled irrigation (NFI) was applied in three replications, with flooding irrigation as a control. Samples of soil, soil solution, irrigation water, and rice plants were collected. Fresh soil samples were digested using the modified European Community Bureau of Reference sequential extraction procedure and the dried crop samples digested at 160 °C using concentrated $HNO_3$. Cu contents in irrigation water, soil solution, extraction for different binding fractions, and the digested solutions were measured using inductively coupled plasma optical emission spectrometry. Leaching loss of Cu was calculated based on the Cu contents in 47- to 54-cm soil solutions and deep percolation rates, which were calculated using the field water balance principle.

*Results and discussion* NFI led to multiple dry–wet cycles and high soil redox potential in surface soil. The dry–wet cycles in NFI soil resulted in higher Cu contents in acid-extractable and oxidizable forms and lower Cu in residual form. High decomposition and mineralization rates of soil organic matter caused by the dry–wet cycles partially accounted for the increased Cu in acid-extractable form in NFI soils. The frequently high contents of Cu in reducible form in NFI fields might be due to the enhanced transformation of Fe and Mn oxides. As a result, Cu uptakes in NFI fields increased by 8.1 %. Meanwhile, Cu inputs by irrigation and loss by leaching in NFI fields were reduced by 47.6 and 46.6 %.

*Conclusions* NFI enhanced the transformation of Cu from residual to oxidizable and acid-extractable forms. The oxidizable form plays a more important role than the reducible form in determining the transformation of Cu from the immobile to the mobile forms in NFI soils. NFI helps improve availability and decreases leaching loss of Cu as a micronutrient in a non-polluted paddy soil, but leads to a high concentration of Cu in rice.

**Keywords** Binding form · Bioavailability · Copper · Dry–wet cycles · Leaching · Water-saving irrigation

## 1 Introduction

Copper (Cu) is an essential micronutrient for plants which is involved in several enzyme systems, cell wall formation, electron transport, and oxidation reactions (Huang et al. 2012). Cu is also regarded as a toxicant at high concentrations to plant cells due to its potential inhibitory effects against many physiological and biochemical processes (Tie et al. 2012). The accumulation of Cu in grains is also directly related to food safety (Xu et al. 2006). Improper use of Cu-enriched materials (such as chemical fertilizer and pesticides, Cu-based fungicides, industrial effluents, sewage sludge, and wastewater) in agriculture leads to Cu contamination of soils. Many researchers investigated crop uptake and enrichment in Cu-polluted soil or soil with high Cu

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inputs using Cu-enriched materials (i.e., (Luo et al. 2003); (Xu et al. 2006); (Bhattacharyya et al. 2006); (Wang et al. 2009); (Liu et al. 2010); (Guan et al. 2011)). The mobility, bioavailability, and toxicity of metals in soil are determined by its binding forms ((Aydinalp & Marinova 2003); (Zheng & Zhang 2011)), which are associated with soil properties including pH, cation exchange capacity, oxidation–reduction status, contents of organic matter, calcium carbonate, and Fe and Mn oxides ((Han et al. 2001); (Chaignon et al. 2009); (Inaba & Takenaka 2005); (Zheng & Zhang 2011)).

Paddy rice is one of the most important cereal crops in Monsoon Asia (Kyuma 2004). The rice fields are generally under saturated conditions, and heavy metals in flooded paddy soil are mostly present in the less labile fractions combined with solid phase components ((Han & Banin 1999); (Zheng & Zhang 2011); (Zhu et al. 2012)). To cope with the increasing water scarcity, water-saving irrigation techniques for rice such as non-flooding controlled irrigation (NFI), alternate dry–wet irrigation, and the system of rice intensification have been developed and applied widely in recent decades ((Mao 2001); (Bouman et al. 2007)). This resulted in multiple dry–wet cycles in paddy fields and a huge change in soil properties, which consequently influenced the biological and chemical processes in soils (Mao 2002). These differences led to changes in the transformation and repartitioning of the heavy metal Cu in soil and its availabilities as both a micronutrient and a toxic metal to rice plants. Unsaturated soil moisture conditions and drying (air drying, oven drying) processes always result in the high mobility and bioavailability of Cu in soils ((Tack et al. 2006); (Biasioli et al. 2010); (Koopmans & Groenenberg 2011); (Zheng & Zhang 2011)). However, little information is available on the binding forms, bioavailability, and fate of Cu in non-polluted paddy fields with different irrigation management. The objectives of this study were to identify the influence of irrigation management on the binding forms of Cu in non-polluted paddy soils and to reveal the fate of copper in paddy soil with different irrigation managements.

## 2 Materials and methods

### 2.1 Site description and experimental design

The experiments were conducted in 2011 on the rice fields at Kunshan irrigation and drainage experimental station (31°15′15″ N, 120°57′43″ E) in the subtropical monsoon climate region of China. The study area has an average annual air temperature of 15.5 °C and a mean annual precipitation of 1,097.1 mm. The top soil texture is clay, with an organic carbon content of 12.9 g $kg^{-1}$, total nitrogen of 1.03 g $kg^{-1}$, total phosphorus of 1.35 g $kg^{-1}$, and pH of 6.84 (soil/water, 1:2.5). The average saturated soil water contents (*v*/*v*) for the layers 0–20, 0–30, and 0–40 cm are 52.4, 49.7, and 47.8 %, respectively. The total Cu contents ($HNO_3$–HF–$HClO_4$ digestion; (Lu 1999)) in 0–20, 20–40, and 40–60 cm soils were 28.04, 27.54, and 24.41 mg $kg^{-1}$, which were lower than the limit for the first grade (35.0 mg $kg^{-1}$) of the Environmental Quality Standard for Soils (GB 15618-1995; (MEP (Ministry of Environment Protection of the People’s Republic of China) 1995)). The Cu contents in irrigation water fell in the range of 7.0–10.1 μg $L^{-1}$, which met the requirement ($<0.5$ mg $L^{-1}$) of the Standards for Irrigation Water Quality (GB 5084-2005; (GAQSIQ (General Administration of Quality Supervision & China) 2005)). The variety of rice was japonica rice 9314. It was transplanted with 25×13-cm hill spacing on June 28 and harvested on October 25, 2011.

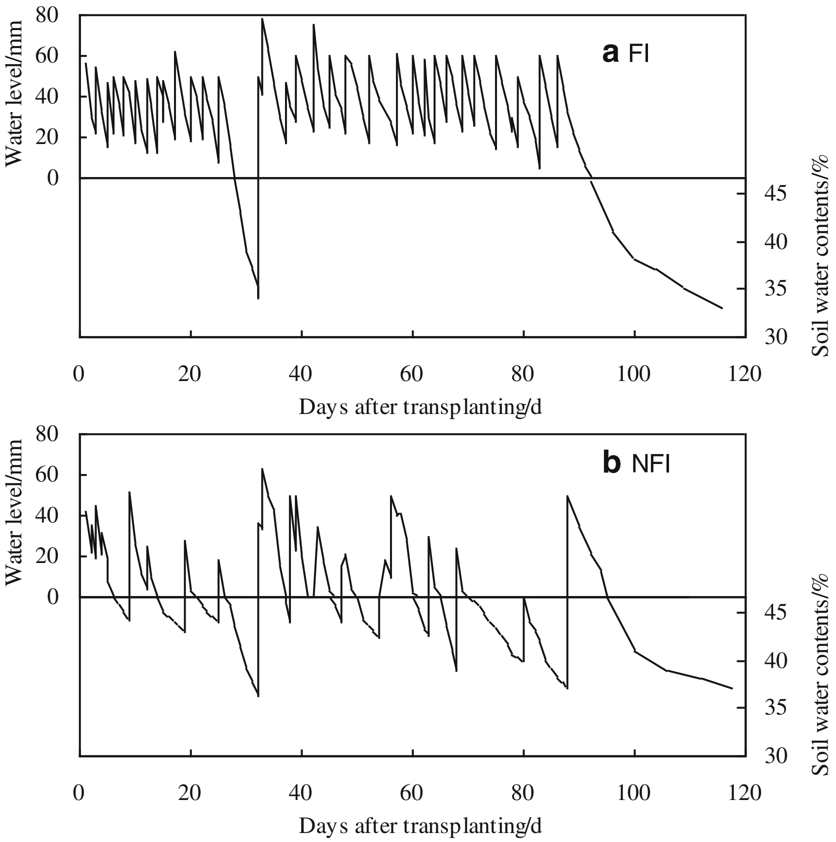
There were two irrigation treatments: flooding irrigation (FI) and non-flooding controlled irrigation (NFI). A randomized complete block design and three replications were established in six plots ($20\times7$ m$=140$ $m^2$). In FI fields, a depth of 3- to 5-cm standing water was always maintained after transplantation, except during the mid-season and harvest drainage period. In NFI fields, the flooding water depth was kept between 5 and 25 mm during the first 7–8 days after transplantation in the regreening stage; irrigation was applied only to keep the soil saturated but not flooded in other stages, except during the periods of pesticide or fertilizer application. In NFI, flooded water up to 5-cm depth was maintained for <5 days when pesticides or fertilizer was applied. The typical field water depth and soil moisture in the FI and NFI fields are shown in Fig. 1. The same doses of fertilizers in three splits were applied to each rice field, in agreement with the local conventional fertilizer application methods.

### 2.2 Field measurements and sample analysis

Irrigation water volume was recorded using a water meter installed on the pipe at the inlet of each plot. Water layer depth was measured using a vertical ruler fixed in the field. The soil moistures in the rice fields were monitored with three replications using a time domain reflectometer (TDR, Soil Moisture, USA) and 20-cm waveguides installed vertically at 0- to 20- and 20- to 40-cm depths. The soil redox potentials ($E_h$) at a 5-cm depth were measured in situ using an oxidation–reduction potential meter. The drainage volume was determined by the water layers before and after drainage. The amount of rainfall was recorded daily using an automatic weather station (ICT, Australia).

Soil solutions were collected using MS22/32 suction cups (Nantong Zhongtian, China) installed vertically at 7- to 14-, 27- to 34-, and 47- to 54-cm depths. The suction cups are made of clay materials (2 cm in inner diameter, 7 cm in length). Irrigation water samples were collected routinely. Water samples were kept in polyethylene bottles and stored

**Fig. 1** Typical field flooding water depth and soil moisture in FI and NFI fields



at 4 °C until analyses. Triplicate soil samples of soil depths of 0–20, 20–40, and 40–60 cm were collected randomly following an S-shaped sampling pattern on August 29 and October 26. The soil samples were stored in a freezer before they were analyzed. Plant samples were randomly taken from the plots on October 26 and divided into four parts (root, stem, leaf and sheath, and spike). They were oven-dried to a constant weight at 65 °C. The dry weights were recorded and the dried subsamples were ground to pass through a 1-mm sieve as the Cu concentrations were determined.

Irrigation water and soil solution samples were filtered using a 0.45-μm Millipore filter and acidified with two to three drops of nitric acid. The dried crop samples (0.5 g) were digested at 160 °C in a polyvinyl fluoride crucible with 4 mL of concentrated $HNO_3$. To avoid transformation of metals during the drying process, as indicated by Shuman (1980) and (Tang et al. 2011)), fresh wet soil samples were used for binding form analysis. The fresh soil samples were divided into two parts: one part (approximately 10 g in dry weight) was used to determine the soil moisture content using the oven-dried method at 105 °C and another part of the fresh soil (approximately 1 g in dry weight) was used for the extraction of different binding forms (0.11 mol $L^{-1}$ acetic acid extractable (EXT), reducible (RED), oxidizable (OXD), and residual (RES) forms) of Cu using the modified European Community Bureau of Reference sequential extraction procedure (Long et al. 2009), with 0.11 mol $L^{-1}$ acetic acid, 0.1 mol $L^{-1}$ hydroxylamine hydrochloride, 8.8 mol $L^{-1}$ hydrogen peroxide, and $HNO_3$–HF–$HClO_4$ as extraction agents. Then, the Cu contents per dry weight of soil in different forms were calculated from the contents in fresh soil and the moisture content. The Cu contents in the irrigation water samples, soil solutions, soil extraction of the different binding fractions, and the digested samples of dry plants were measured using inductively coupled plasma optical emission spectrometry (Thermo ICAP 6000 duo, Thermo Scientific).

## 2.3 Leaching loss of Cu

Seasonal leaching loss of Cu was calculated based on the Cu contents in 47- to 54-cm soil solutions and deep percolation rates (DP). The daily DP rate was calculated using the water balance principle (Eq. 1) based on field measurements during the rice season.

$$\mathrm{DP}_t = W_{t-1} - W_t + I_t + P_t - D_t - \mathrm{ET}_t \tag{1}$$

where DP is the percolation rate; $W$ is the flooding water depth or soil water content in the root zone; $I$, $P$, and $D$ are water volumes of irrigation, precipitation, and drainage, respectively; and ET is the evapotranspiration, which was measured using the water balance principle based on the water balance measurement in bottom-sealed lysimeters (40 cm in diameter and 60 cm in depth with four hills of rice planted inside) with the same irrigation management as in the plots. Figure 2 shows the cumulative water depths of *I*, *P*, ET, and DP.

## 3 Results

### 3.1 Water consumption, rice yields, and soil redox potentials

There were 12 wet–dry cycles in NFI fields, with more than 65 days under the non-flooding or unsaturated condition (see Fig. 1). This led to reduced rice water consumption in NFI. The evapotranspiration and deep percolation were 581.7 and 291.1 mm in NFI fields, respectively, reduced by 17.6 and 30.9 % compared with the FI treatment (Table 1). Consequently, the irrigation volume in NFI fields was reduced by 50.8 %. Meanwhile, rice yield was 8,103.1 kg ha$^{-1}$ for NFI treatment and increased by 5.2 % compared with FI treatment. Input of Cu by irrigation to paddy soil was 29.40 g ha$^{-1}$ in NFI paddies, which was reduced by 47.6 % compared with FI paddies (56.09 g ha$^{-1}$). The differences in irrigation volume and its Cu input, evapotranspiration, and deep seepage were significant ($p<0.05$) between NFI and FI treatments. Multiple dry–wet cycles in the NFI fields also led to a change in soil redox conditions (Fig. 3). For most of the rice season, $E_h$ values in NFI fields were significantly higher than those in FI fields.

### 3.2 Binding forms of Cu in soils

Generally, the total Cu contents in 0- to 20-cm surface soil were higher than in deep soil, and the Cu in each form was in the order of RES>OXD>RED>EXT (Table 2). But most of the differences are insignificant at $p<0.05$ by Tamhane's test. The RES form of Cu accounted for more than half of the total Cu in paddy soils. The EXT fraction of Cu, which was the most labile and easily available to crops, was the lowest and was <2 % of the total Cu contents. Compared with soils under flooding condition, Cu in EXT, RED, and OXD forms in surface soils were higher in NFI; Cu in RES form was lower. However, only the difference in acid-extractable fraction between FI and NFI is significant at $p<0.05$.

### 3.3 Cu in soil solutions and its leaching risks

In the current research, Cu contents in soil solutions ranged from 2.5 to 12.0 μg L$^{-1}$ (Fig. 4), with almost the same range as Cu contents in irrigation water (7.0–10.1 μg L$^{-1}$). The Cu contents in soil solutions were low according to the Quality Standard for Groundwater GB/T 14848-93 (GAQSIQ (General Administration of Quality Supervision & China) 1993). The Cu contents in soil solutions were higher in the former than in the latter part of the growth season, which implied that outputs of Cu by crop uptake and leaching were greater than inputs in rice fields. The same conclusion can be drawn when comparing the soil Cu contents in later season with those in mid-season (see Table 2). As a result of the increased EXT form of Cu in NFI paddy soils, the Cu contents in surface 7- to 14-cm soil solutions were mostly slightly higher in NFI than in FI (see Fig. 2). Additionally, due to less percolation in NFI fields, Cu contents in deep soil solutions in NFI were mostly lower than those in FI fields. According to the Wilcoxon signed-rank test for paired data, the significance values of Cu in soil solutions between NFI and FI treatments are 0.123, 0.959, and 0.203 in depths of 7–14, 27–34, and 47–54 cm, respectively. The differences of Cu in soil solutions between NFI and FI treatments are insignificant. Because NFI resulted in a reduction both in deep percolation rate and Cu contents in deep soil solutions, the leaching risk of Cu into groundwater in NFI fields was much lower than that in FI fields. The seasonal leaching loss of Cu from NFI fields was summed as 8.81 g ha$^{-1}$ and reduced significantly by 46.6 % compared with that from FI fields (16.50 g ha$^{-1}$).

### 3.4 Plant uptakes of Cu

The Cu contents in root, leaf and sheath, stem, and spike were 3.40, 1.56, 2.55, and 0.75 mg kg$^{-1}$ in NFI rice plants,

**Table 1** Rice yields and water consumption with different irrigation managements

| Treatment | Yield (kg ha$^{-1}$) | Irrigation (mm) | Cu input by irrigation (g ha$^{-1}$) | Evapotranspiration (mm) | Water consumption (mm) | Deep seepage (mm) |
|---|---|---|---|---|---|---|
| NFI | 8,103.1a | 371.6a | 29.40a | 581.7a | 872.8a | 291.1a |
| FI | 7,705.9a | 754.4b | 56.06b | 706.1b | 1127.3b | 421.2b |

Different letters in each column represent significant difference between treatments at $p=0.05$ with Tamhane's test

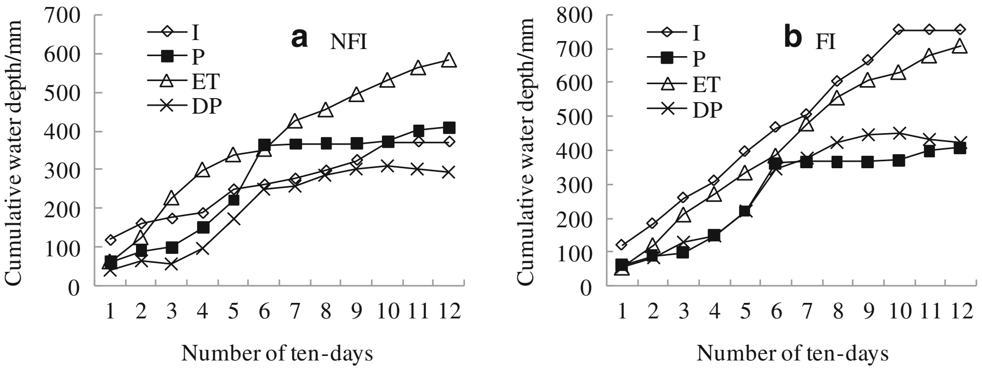


**Fig. 2** Cumulative water depths of irrigation (*I*), precipitation (*P*), evapotranspiration (*ET*), and percolation (*DP*)

higher than those in FI rice plants. But the differences between NFI and FI were insignificant, except for Cu contents in root. Cu contents in roots and stems were higher than in leaf and spike (Table 3). Total crop uptakes and uptakes in aboveground parts in NFI fields were 36.13 and 25.15 g ha$^{-1}$ and increased by 11.2 and 8.1 %, respectively, than in FI fields. It confirmed that NFI enhanced the bioavailability of soil Cu. Other than the high availability of Cu, high root absorption ability also partially accounted for high crop absorption ability under dry–wet cycle conditions. This phenomenon was also reported for other metals when the flooding condition was replaced by aerobic or dry–wet cycle conditions in rice paddies ((Ji et al. 2007); (Yang et al. 2009)). Because the Cu level is very low in the paddy soils and irrigation water, the Cu contents in rice spike are as low as 0.65 and 0.75 mg kg$^{-1}$ in FI and NFI fields, respectively. The Cu contents in rice seeds are much lower than the limit of Cu in food (Ministry of Health of the People's Republic of China (MOH) 1994) in the current research, but if the soil or irrigation water was Cu-polluted, NFI may lead to a greater risk of Cu pollution in rice seeds compared to FI.

## 4 Discussions

### 4.1 Change in the binding forms of Cu in soil

The EXT fraction of Cu would be released into the environment if conditions became more acidic. It is the fraction with the highest availability (Long et al. 2009). Cu in EXT form was higher in NFI than in FI in the 0- to 20- and 20- to 40-cm soils, but lower than FI in 40- to 60-cm deep soils (see Table 2). This indicated that drying or dry–wet cycles might increase the solubility of Cu in surface soils, as indicated by other studies ((Tack et al. 2006); (Biasioli et al. 2010); (Koopmans & Groenenberg 2011)). The highly reduced deep percolation in NFI fields led to a less downward movement of soluble Cu from surface to deep soils, although the mobilization of Cu in surface soils increased. Because the Cu concentrations in the paddy soil and irrigation water were low in the current experiments, high contents of the EXT forms of Cu in NFI paddies were helpful in improving its availability to rice plants as a micronutrient. But if in paddies with Cu-enriched soil or irrigated with Cu-

**Table 2** Concentrations of Cu in different sequential extraction fractions in paddy soil under different irrigation managements (in milligrams per kilogram)

| Sampling data | NFI | | | | | FI | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | EXT | RED | OXD | RES | Sum | EXT | RED | OXD | RES | Sum |
| 29 August | | | | | | | | | | |
| 0–20 cm | 0.57a* | 5.40a | 6.92a | 14.30a | 27.19a | 0.33a | 5.30a | 6.41a | 15.70a | 27.74a |
| 20–40 cm | 0.33b* | 4.52a | 6.58a | 15.58a | 26.99a | 0.21b | 4.48a | 6.47a | 16.05a | 27.21a |
| 40–60 cm | 0.38b | 5.43a | 4.78b | 14.55a | 25.15a | 0.36a | 5.01a | 4.27b | 15.55a | 25.19a |
| 26 October | | | | | | | | | | |
| 0–20 cm | 0.47a* | 4.43a | 7.48a | 14.73a | 27.11a | 0.20a | 4.54a | 7.27a | 15.15a | 27.22a |
| 20–40 cm | 0.33b | 4.61a | 7.38a | 14.55a | 26.87a | 0.29a | 4.54a | 7.71a | 14.57a | 27.11a |
| 40–60 cm | 0.44a | 5.64b | 3.30b | 14.15a | 23.53a | 0.55b | 5.48a | 3.19b | 14.46a | 23.68a |

Different letters in each column represent significant difference between depths at $p=0.05$ with Tamhane's test

*EXT* acid extractable, *RED* reducible, *OXD* oxidizable, *RES* residual

*Value in NFI treatment which was significantly different from the relevant value in FI treatment at $p=0.05$ with Tamhane's test

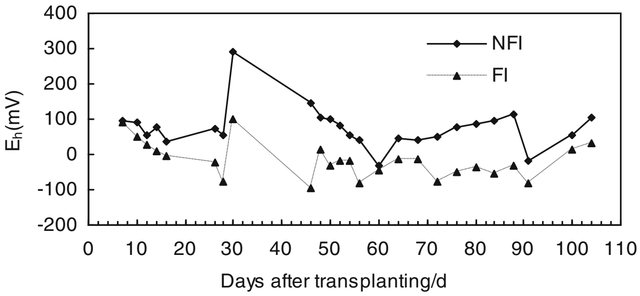


**Fig. 3** Soil redox potentials at 5-cm depth

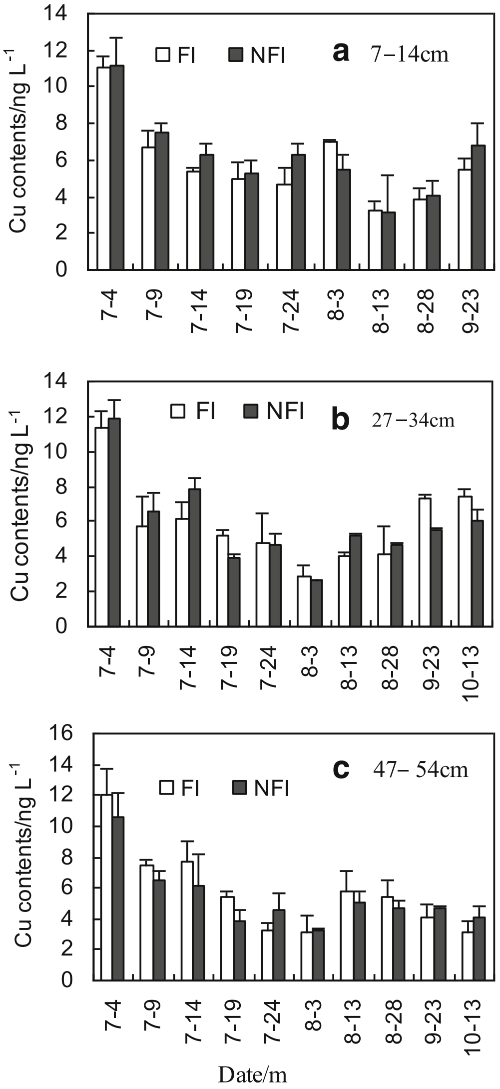


**Fig. 4** Contents of Cu in soil solution at depths of 7–14 cm (**a**), 27–34 cm (**b**), and 47–54 cm (**c**)

polluted water, the increased availability of Cu in NFI might lead to a high risk of Cu absorption by plants.

Accompanied with the increase in the EXT form of Cu in NFI soils, the RED forms (combined with iron or manganese oxides) of Cu in soil at different depths were frequently increased compared with FI soils, but RES forms of Cu were decreased (see Table 2). The OXD fraction, which is said to be bound to sulfurs or soil organic matter (SOM), would be expected to be released into the environment when the sulfide minerals and SOM were dissolved due to oxidization under the drying or dry–wet cycle conditions ((Arao et al. 2010); (Tang et al. 2011); (Koopmans & Groenenberg 2011)). However, contrary to expectations, the OXD form of Cu in NFI soils was not decreased in the current experiment, but increased insignificantly. This may be ascribed to the release of the RES form in NFI soils, which can be confirmed partially as the reduction of Cu in RES form, as indicated in Table 2.

Cu in paddy soil is presented in various forms including ion, precipitated minerals, complexes with ligands, and inorganic and organic colloidal species. In flooded soil, ion of $Cu^{2+}$ which is more easily available can be reduced to $Cu^{+}$ by reductants of $Fe^{2+}$ or $H_2S$ and reduced to elemental forms by $Fe^{2+}$-bearing green rust ((Borch et al. 2010); (Violante et al. 2010)). It can also be precipitated as CuS or be co-precipitated with FeS and MnS. When the continuous flooding condition was replaced by the dry–wet cycles in NFI fields, the anaerobic conditions were brought to a close; the soil $E_h$ increased greatly (as in Fig. 3). There will be less reductants (such as $Fe^{2+}$ and $S^{2-}$) in NFI soils and less $Cu^{2+}$ will be reduced. Cu co-precipitated with FeS and MnS are oxidized in soils under aerobic conditions (Eggleton & Thomas 2004). SOM, especially the dissolved organic matter (DOC), is another main component of the soil and has been shown to be highly related to the mobility of metals in soil ((Inaba & Takenaka 2005); (Khan et al. 2006); (Kelderman & Osman 2007); (Vandecasteele et al. 2007); (Zeng et al. 2011); (Koopmans & Groenenberg 2011)). It has been stated that practically every chemical aspect of heavy metals in soils is related to the formation of complexes with low-molecular-weight organic acids (Dube et al. 2001). Copper mainly exists as dissolved organic matter (DOM) complexes in soils and is known to bind more strongly to humic substances to form Cu–DOM complexes than other metals ((Temminghoff et al. 1997); (Brazauskiene et al. 2008)). Under the dry–wet cycle condition in NFI fields, the decomposition and mineralization rates of SOM were enhanced and soil DOC increased ((Klitzke 2007); (Koopmans & Groenenberg 2011); (De Palma et al. 2011)). High soil DOC contents might account for the increase in soil-soluble Cu in NFI soils, as indicted under dry–wet cycle conditions ((Klitzke & Lang 2007); (Amery et al. 2007); (Lin et al. 2010); (Koopmans & Groenenberg 2011)). Thus, the reduction of the RES form of Cu in NFI soils is partially attributable to less Cu being transformed from the labile to the less labile fractions and also ascribed to more Cu in the R fraction being transformed to other forms under dry–wet cycle conditions.

**Table 3** Contents and uptakes of copper in different parts of rice plants

| Treatment | | Root | Leaf and sheath | Stem | Spike | Total | Aboveground |
|---|---|---|---|---|---|---|---|
| Cu contents (mg $kg^{-1}$) | FI | 2.95a | 1.55a | 2.43a | 0.65a | – | – |
| | NFI | 3.40b | 1.56a | 2.55a | 0.75a | – | – |
| Cu uptake (g $ha^{-1}$) | FI | 9.22a | 12.54a | 6.20a | 4.53a | 32.49a | 23.27a |
| | NFI | 10.98b | 13.06a | 6.67a | 5.43a | 36.13a | 25.15a |

Different letters in each column represent significant difference between treatments at $p$=0.05 with Tamhane's test

Redox condition also controls the transformation and reactivity of Fe and Mn oxides in soils, which have large sorption capacities for trace metals and are major sinks for heavy metals and metalloids (Tack et al. 2006). In flooded soil, Fe and Mn are mostly present in amorphous forms. Drying processes or dry–wet cycles enhanced the transformation of Fe and Mn from amorphous oxides to more crystalline forms, which can immobilize trace metals ((Zhang et al. 2003), (Zhang et al. 2006); (Thompson et al. 2006); (Koopmans & Groenenberg 2011)). That would lead to a stronger binding of the Cu and, hence, decrease the concentrations of Cu in the EXT form and increase the RED form. However, the EXT form of Cu increased in NFI soils. This implies that OXD forms may play a more important role than the RED form in determining the transformation from the immobile to the mobile forms of Cu in NFI paddy soils. The high solubility of SOM caused by the dry–wet cycles mostly explains the increased levels of Cu in EXT form in NFI soils. This may also be ascribed to the dry–wet cycles in the NFI paddy which function differently from drying or continuously moist soil due to the burst of microbial activity which occurs under dry–wet cycle conditions ((Bartlett & James 1980); (Tack et al. 2006)). Thus, the change of the binding forms of Cu in NFI fields is ascribed to the high soil $E_h$, the high decomposition and mineralization rates of SOM, and the formation of Cu–DOM complexes under dry–wet cycle conditions.

## 4.2 Downward movement and leaching risk of Cu in soil solution

The downward movement of soluble metals from surface soils to deep soils or groundwater has been previously monitored in landfill or compost sites ((Kaschl et al. 2002); (Chen et al. 2010)), but there is little information on metals leaching in rice fields with different irrigation managements. In the current research, the leaching loss of Cu was an important pathway of Cu output in both NFI and FI fields, accounting for about 30 % of Cu inputs by irrigation. The Cu concentrations in 7- to 14-cm surface soil solutions in NFI fields were slightly higher than those in FI fields (see Fig. 4), with the concentrations almost the same as the Cu in irrigation water. The increased acetic acid-extractable Cu only led to a slight increase of Cu in surface soil solutions. At the same time, Cu concentrations in 47- to 54-cm soil solutions in NFI fields were mostly lower than in FI fields (see Fig. 4). It implies that s largely reduced deep percolation rate and increased crop uptakes decreased the downward movement and leaching risks of Cu in NFI fields. The leaching loss reduction rate of Cu in NFI fields was 46.6 %, higher than the reduction rate of deep seepage volume (30.9 %). It indicates that reduction of deep seepage volume might take a more important role than the reduction of Cu concentration in deep soil solutions when determining the reduced leaching losses of Cu.

## 4.3 Potential effect on soil, food, and groundwater pollution

In the current research, NFI can help reduce the loss of Cu due to leaching and risk of groundwater pollution and improved availability of Cu as a micronutrient. Thus, in the case that soil and water are non-polluted by Cu, NFI may play an active role in improving micronutrient availability and coping with Cu pollution of soil, food, and groundwater. Because NFI reduced the irrigation input of Cu (see Table 1) and enhanced soil Cu mobility and crop uptakes (see Tables 2 and 3), this led to less Cu accumulation in soils (see Table 2). At the same time, it reduced the risk of groundwater Cu pollution by cutting down the leaching losses of Cu (see Fig. 4). However, long-term application of NFI might lead to soil Cu deficit. If the soil or irrigation water is Cu-polluted, NFI might result in the higher risk of food Cu pollution in the short term, but in long term, it will lower the accumulation of Cu in NFI soils and eventually reduce crop Cu uptakes.

## 5 Conclusions

Cu was mostly present in the RES forms in paddy soil, followed by the OXD and RED forms. The EXT fraction of Cu was the smallest. Multiple dry–wet cycles in NFI fields led to high soil redox potentials and, hence, the change in Cu binding forms, leaching risks, and crop uptakes. The Cu contents in EXT form were higher in NFI than in FI in the 0- to 20- and 20- to 40-cm soils, but lower than FI in 40- to 60-cm deep soils. At the same time, the RED and OXD forms of Cu in different soil depths were mostly increased compared with FI soils, but the RES form of Cu was decreased. It implied that NFI enhanced the transformation of Cu from the RES to the OXD and EXT forms. The OXD form plays a more important role than the RED form in determining transformation from the immobile form to the mobile form of Cu in NFI paddy soils. The high decomposition and mineralization rates of SOM caused by the dry–wet cycles partially accounted for the increased levels of Cu in EXT form in NFI soils. The frequently high contents of Cu in RED form in NFI fields might be attributed to the enhanced transformation of Fe and Mn from amorphous metal oxides to more crystalline forms under dry–wet cycle conditions. In paddy soil with low copper content, NFI can help improve the availability of Cu as a micronutrient, resulting in higher plant uptakes of Cu and reduced loss of Cu by leaching. However, if the soil or irrigation water was polluted by Cu, NFI may lead to a higher risk of Cu pollution in rice seed than FI.

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