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RESEARCH ARTICLE

Field evidence of decreased extractability of copper and nickel added to soils in 6-year field experiments

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HIGHLIGHTS

- Long-term decrease in added Cu and Ni toxicity was easily identified in neutral soil.
- Extractability as an aging indicator of Cu and Ni is better than phytotoxicity.
- In neutral and alkaline soil Cu is extractable more than Ni.
- In acidic soil extractability of Cu is similar to Ni.

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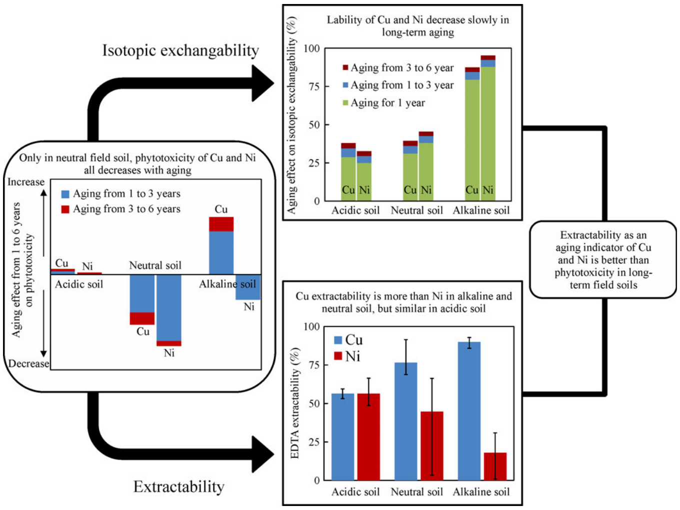
GRAPHIC ABSTRACT



ABSTRACT

The phytotoxicity of added copper (Cu) and nickel (Ni) is influenced by soil properties and field aging. However, the differences in the chemical behavior between Cu and Ni are still unclear. Therefore, this study was conducted to investigate the extractability of added Cu and Ni in 6-year field experiments, as well as the link with their phytotoxicity. The results showed that the extractability of added Cu decreased by 6.63% (5.10%–7.90%), 22.5% (20.6%–23.9%), and 6.87% (0%–17.9%) on average for acidic, neutral, and alkaline soil from 1 to 6 years, although the phytotoxicity of added Cu and Ni did not change significantly from 1 to 6 years in the long term field experiment. Because of dissolution of Cu, when the pH decreased below 7.0, the extractability of Cu in alkaline soil by EDTA at pH 4.0 could not reflect the effects of aging. For Ni, the extractability decreased by 18.1% (10.1%–33.0%), 63.0% (59.2%–68.8%), and 22.0% (12.4%–31.8%) from 1 to 6 years in acidic, neutral, and alkaline soils, respectively, indicating the effects of aging on Ni were greater than on Cu. The sum of ten sequential extractions of Cu and Ni showed that added Cu was more extractable than Ni in neutral and alkaline soil, but similar in acidic soil.

1 Introduction

The average annual input of Cu and Ni to agricultural soils in China was 0.21 mg/kg and 0.03 mg/kg, respectively. According to Luo et al. [1], about 68.54% of Cu inputs was from livestock manures, 67.47% of Ni inputs was from atmospheric deposition. The environmental and health effects of soil contaminated with heavy metals depend on the processes of the contaminant immobilization [2]. Moreover, the partition and exchange of heavy metals between soil solid and solution phases are essential to

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understanding the extractability and bioavailability of heavy metals [3]. When water-soluble heavy metals are added to soils, the metals rapidly partition between the soil solution and solid phases, after which their extractability and bioavailability continue to decrease slowly over time [4]. Zhou et al. [5] used a sequential extraction procedure to investigate the aging of copper (Cu) added to bentonite and found that the most labile Cu fractions decreased over time. The adsorption of Cu in soils reached equilibrium during the initial fast stage, while the subsequent reactions were slower due to the diffusion or the formation of surface precipitation [6]. In the case of nickel (Ni), Scheidegger and Sparks [7] studied the kinetics of the formation and dissolution of surface precipitates of Ni on pyrophyllite and found that the slow detachment of Ni was due to the dissolution of mixed Ni-Al hydroxides. The results using X-ray absorption spectroscopy showed that Ni sequestration in soils was dominated by Ni adsorption on soil organic matter (OM) in 24 h, as well as by Ni layered double hydroxides (Ni-LDH) precipitates in the first month, and that over time, the adsorbed Ni is probably transformed gradually into the Ni-LDH phase [8,9]. Ma et al. [10–12] developed semi-mechanistic models of short-term and long-term aging of water-soluble Cu and Ni added to European soils and the results suggested that the lability of Cu and Ni is attenuated by three processes: precipitation or nucleation on soil surfaces, occlusion within OM, and diffusion into micropores.

With aging, the extractability of heavy metals decreases [13]. As an effective extractant, ethylenediaminetetraacetic acid (EDTA) was applied to evaluate metal extractability or availability in many laboratory studies [14,15]. The efficiency of EDTA extraction differs with differences in the lability of heavy metals, the strength of EDTA, and soil properties [16–18]. Sun et al. [19] conducted batch extraction with EDTA and found that the mobility of Zn and Cd was usually slightly lower than that of Cu. Scheckel and Sparks [15] reported that EDTA at pH 4.0 released more Ni from the precipitates than EDTA at pH 7.5 because, at higher pH, EDTA may be competing with OH^- ions for metal binding sites. Tsang et al. [20] used EDTA as a reference chelating agent in column experiments to investigate the effectiveness of chelant-enhanced flushing of artificially contaminated soils and found that a large portion of Cu was extracted from the oxides, OM, and residual fractions.

Many laboratory studies have shown that phytotoxicity and bioavailability of heavy metals decreases with time because of the decreased extractability during long-term processes [21,22]. To assess the phytotoxicity and risk of soils contaminated by heavy metals, it is critical that the time-dependent desorption behavior and species of heavy metals be understood clearly. However, lack of experimental data from field-contaminated soils has limited our understanding of the bioavailability of heavy metals in the long term. Therefore, in the present study, we utilized soil samples from three field soils that had been contaminated for a long time (6 years) to study the phytotoxicity and processes of Cu and Ni release from contaminated soils, which were measured by ten sequential extractions of EDTA at three pH values (pH 4.0, pH 6.0, and pH 7.5). The phytotoxicity and extractability of Cu and Ni were also compared to obtain a better aging indicator.

2 Materials and methods

2.1 Soil samples and treatments

Topsoil samples (0–20 cm) of acidic, neutral, and alkaline field contaminated soils were obtained from long-term experiment stations of the China Academy of Agricultural Sciences. The field soil properties are shown in Table 1. The experiment for Cu or Ni in each field soil consisted of eight application rates of either Cu or Ni: 0, 12.5, 25, 50, 100, 200, 400, and 800 mg/kg for acidic soil, 0, 25, 50, 100, 200, 400, 800, and 1600 mg/kg for neutral soil, and 0, 50, 100, 200, 400, 800, 1600, and 3200 mg/kg for alkaline soil. To decrease the variability from spiking, the salts of $CuCl_2$ or $NiCl_2$ were mixed thoroughly with topsoil samples separately in a container, after which the spiked soils were returned to the experimental plots. The field experiments were conducted from 2007 to 2012.

The soil samples were selected from field soils cultivated for 1, 3 and 6 years after metal salts were added. The samples were air-dried and sieved through a 2-mm sieve. Next, the concentrations of total Cu and Ni in soils were measured using an *aqua regia* (a fresh mixture [1:3] of

Table 1 Soil properties and background concentration of Cu and Ni in three field soils

Soils	pH[a]	CEC[b]	OC[c]	$CaCO_3$	OX[d] Fe	CD[e] Fe	OX[d] Al	CD[e] Al	Cu	Ni
	(1:5)	(cmol^+/kg)	(%)	(%)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Acidic soil (QY-pH 5.3)	5.3	7.47	0.87	0.09	1146.4	26,154	1326	3293	29.4	22.3
Neutral soil (JX-pH 6.7)	6.7	19.33	1.42	0.15	6211.8	10,824	1106	794	30.8	32
Alkaline soil (DZ-pH 8.9)	8.9	8.33	0.69	6.17	644.2	4965	497	369	24.6	20.2

Notes: a) Measured in deionized water (1 part soil mixed with 5 parts water, by volume) [23]; b) Cation exchange capacity determined using the ammonium chloride method [23]; c) Organic carbon, determined as the difference between total and inorganic carbon contents [24,25]; d) Oxalate extractable metal [26,27]; e) Citrate dithionate extractable metal [28,29] concentrated HNO_3 and HCl) digestion, followed by atomic absorption spectroscopy (ZEEnit 700, Analytik Jena, Germany) according to Zarcinas et al. [30]. A geochemical standard reference soil (GSS-16) (GBW-07430, China National Center for Standard Materials) was used as a certified reference material. Certified concentrations in the reference material never differed by more than 10% from the measured concentrations. All treatments were replicated 3 times.

2.2 Determination of Cu and Ni phytotoxicity in field soils

According to the typically used local farming practice, we selected maize for acidic (QY-pH 5.3) and alkaline soil (DZ-pH 8.9) and rice for neutral soil (JX-pH 6.7) to indicate the phytotoxicity of Cu or Ni in field soils. The phytotoxicity thresholds were expressed as the effective concentrations of Cu or Ni causing 50% inhibition in crop growth (EC50-Cu or EC50-Ni). The EC50 values, along with their 95% confidence intervals, were derived from the fitted dose–response model parameters and standard errors in Microsoft Excel according to Haanstra et al. [31]:

$$Y = \frac{Y_0}{1 + e^{b(X-M)}}, \tag{1}$$

where, Y is relative crop growth (%), X is $\log_{10}$ of the concentration of added Cu or Ni (mg/kg), M is the $\log_{10}$ of the EC50-Cu or EC50-Ni value (mg/kg), and Y_0 and b are curve fitting parameters [31,32]. The measured concentration of added Cu or Ni was used as the metal dose, which is the measured total concentration of each soil minus the average concentration of control treatments. Statistical significance between toxicity thresholds of Cu or Ni added to field soils aged for different years were conducted using SPSS 19.0.

2.3 Extraction of added Cu and Ni in three soils aged for different time

To examine the influence of aging on the extractability of Cu and Ni in three soils over 1, 3, or 6 years, two concentrations based on similar phytotoxicity [33,34] in three soils were selected: a low concentration leading to a decrease in biomass of 10% (50 mg/kg for QY-pH 5.3, 400 mg/kg for JX-pH 6.7, and 800 mg/kg for DZ-pH 8.9) and a high concentration leading to a decrease in biomass of 50% (100 mg/kg for QY-pH 5.3, 800 mg/kg for JX-pH 6.7, and 1600 mg/kg for DZ-pH 8.9). The extractability of Cu or Ni added to soils aged for different time was measured by ten sequential extractions of EDTA and expressed as the proportions (%) relative to total added Cu or Ni in soils (ten-EDTA-Cu or ten-EDTA-Ni).

Soil samples (1 g each, air-dried, < 2 mm) were shaken with 50 mL of EDTA (at pH 4.0, pH 6.0, and pH 7.5) in 100 mL polypropylene centrifuge tubes for 12 h at room temperature (~20°C) in a reciprocating shaker. The soil suspension was centrifuged at about 2000 g for 10 min, after which the supernatant was decanted and filtered through a filter paper (pore size 0.45 μm). A fresh batch of 50 mL of EDTA was then added to the residue. The extraction steps were repeated 10 times over 120 h, which resulted in a stable amount of Cu or Ni remaining on the soil samples. The contents of Cu and Ni in the supernatants in each cycle were determined using atomic absorption spectroscopy (ZEEnit 700, Analytik Jena, Germany). All treatments were replicated 3 times.

3 Results and discussion

3.1 Phytotoxicity of Cu and Ni added to soils aged for different time

A long-term field experiment was conducted to investigate the phytotoxicity of Cu and Ni added to different soils aged for different time (Fig. 1). For Cu, the results showed that the decrease in phytotoxicity was only significant in neutral soil (JX-pH 6.7), for which the EC50 increased by 7.9-fold (132–1180 mg/kg). However, there was no significant difference (T-test at 5% probability level) among 1, 3, and 6 years in acidic soil (QY-pH 5.3), while in alkaline soil (DZ-pH 8.9) the phytotoxicity increased by 1.5-fold. For Ni, the phytotoxicity decreased significantly by 5.8-fold in neutral soil (JX-pH 6.7) and by 0.69-fold in alkaline soil (DZ-pH 8.9), although it increased by 2.7-fold in acidic soil (QY-pH 5.3). Generally, the phytotoxicity of Cu and Ni added to field soils initially decreased quickly, then slowly with aging time [10,12]. The data collected in a report by McBride et al. [35] showed that the Cu availability decreased abruptly in the first year following spiking. According to the calculation of semi-mechanistic models for long-term aging processes, the isotopic exchangeability of added Cu and Ni decreased by 29.2% and 32.6% in the first year, and only decreased by 8.59% and 7.58% from 1 to 6 years, respectively; therefore, there was not a great difference between biological variance and aging effect on phytotoxicity of Cu and Ni in soils, indicating that phytotoxicity should only be used as an indicator for long-term and slow aging effects with caution.

3.2 Extractability of Cu and Ni added to soils aged for different times

The extractability of Cu or Ni added to soils aged for different time was measured by ten sequential extractions of EDTA (ten-EDTA-Cu or ten-EDTA-Ni), which was expressed as the proportions (%) relative to the total added

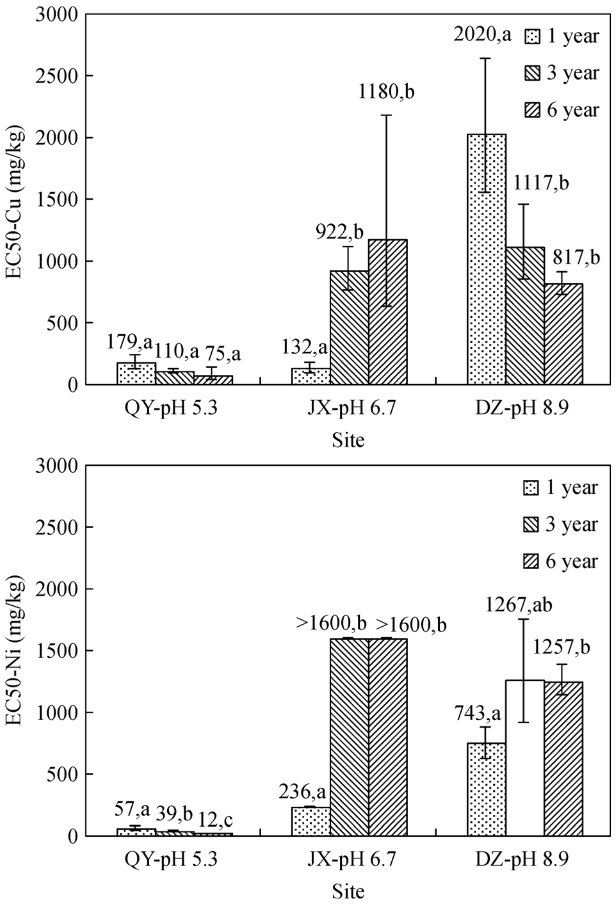

Fig. 1 Toxicity thresholds (EC50) of Cu and Ni added to field soils aged for 1, 3, and 6 years. The crops used to assess the toxicity of Cu and Ni in different soils: maize for acidic soil in Qiyang (QY-pH 5.3) and alkaline soil in Dezhou (DZ-pH 8.9), rice for neutral soil in Jiaxing (JX-pH 6.7). Different letters in the same field soil indicate significant differences among different aging time at $p < 0.05$

Cu or Ni in soils. The results of the ten-EDTA-Cu and ten-EDTA-Ni in three different soils (QY-pH 5.3, JX-pH6.7, and DZ-pH 8.9) aged for 1, 3, and 6 years at three pH values (pH 4.0, pH 6.0, and pH 7.5) of extractant are shown in Table 2.

The results shown in Table 2 indicate that the extractability of added Cu tended to decrease with aging time from 1 to 6 years in three different soils at the three extractant pH values, except for the ten-EDTA-Cu in alkaline soil at an extractant pH of 4.0. The extractability of added Cu in alkaline soil by pH 4.0 EDTA decreased with aging time in the first five sequential extractions (Fig. 2), during which the pH of the soil-EDTA mixture stayed above 7.0 (7.63–8.04). When the pH decreased below 7.0, the extractability of added Cu was stable, possibly due to the dissolution of Cu bound to easily reducible Mn oxide and carbonate. Overall, the extractability of added Cu was decreased by 6.63% (5.10%–7.90%) and 6.87% (0%–17.9%) on average for acidic and alkaline soil. These results were in agreement with the calculations of semi-mechanistic models, which showed that the isotopic exchangeability of added Cu decreased by 8.81% and 8.17% for acidic and alkaline soil. The extractability of Cu in neutral soil decreased by 22.5% (20.6%–23.9%), which was a greater decrease than that obtained by the semi-mechanistic model (8.79%).

The extractability of Ni tended to decrease with aging time from 1 to 6 years in three different soils at three pH values (pH 4.0, pH 6.0, and pH 7.5). From 1 to 6 years, the ten-EDTA-Ni decreased 18.1% (10.1%–33.0%), 63.0% (59.2%–68.8%), and 22.0% (12.4%–31.8%) in acidic, neutral, and alkaline soils, respectively, indicating that the effects of aging expressed by extractability on Ni were greater than on Cu. Non-extractable Ni (total Ni minus EDTA-extractable Ni, Fig. 3) was 51.3% (39.6%–70.4%), 96.5% (94.8%–98.7%), and 99.1% (98.7%–99.7%) on average in acidic, neutral and alkaline soil aged for 6 years, respectively, which were all higher than the isotopic exchangeability decrease (32.9%, 45.8%, and 95.6%) calculated by the semi-mechanistic model [12] based on the precipitation and diffusion process. This likely indicates that the EDTA extractability for Ni is weaker than the Ni isotopic exchangeability in acidic and neutral soil.

The results of ten sequential extractions showed that the extractability of Ni was lower than that of Cu in neutral and alkaline soil, but similar in acidic soil. In acidic soil, the

Table 2 Sum of ten extractable proportions (%) of Cu and Ni by EDTA to total added Cu and Ni in different soils aged for 1, 3, and 6 years

Extractable metal	Soil	pH 4.0			pH 6.0			pH 7.5		
		1 (year)	3 (year)	6 (year)	1 (year)	3 (year)	6 (year)	1 (year)	3 (year)	6 (year)
Ten-EDTA-Cu	Acidic (QY)	64.6	59.4	56.7	54.8	52.0	49.7	59.2	55.8	52.3
	Neutral (JX)	94.1	79.1	73.5	90.6	60.5	66.7	90.0	71.5	66.9
	Alkaline (DZ)	98.5	92.9	98.5	82.2	94.6	79.5	98.4	89.9	80.5
Ten-EDTA-Ni	Acidic (QY)	62.6	50.5	29.6	71.5	57.6	60.4	66.2	-	56.1
	Neutral (JX)	64.4	62.4	5.24	70.1	69.1	1.35	65.1	63.6	3.94
	Alkaline (DZ)	32.8	39.2	1.05	22.2	29.5	0.28	13.7	25.5	1.34

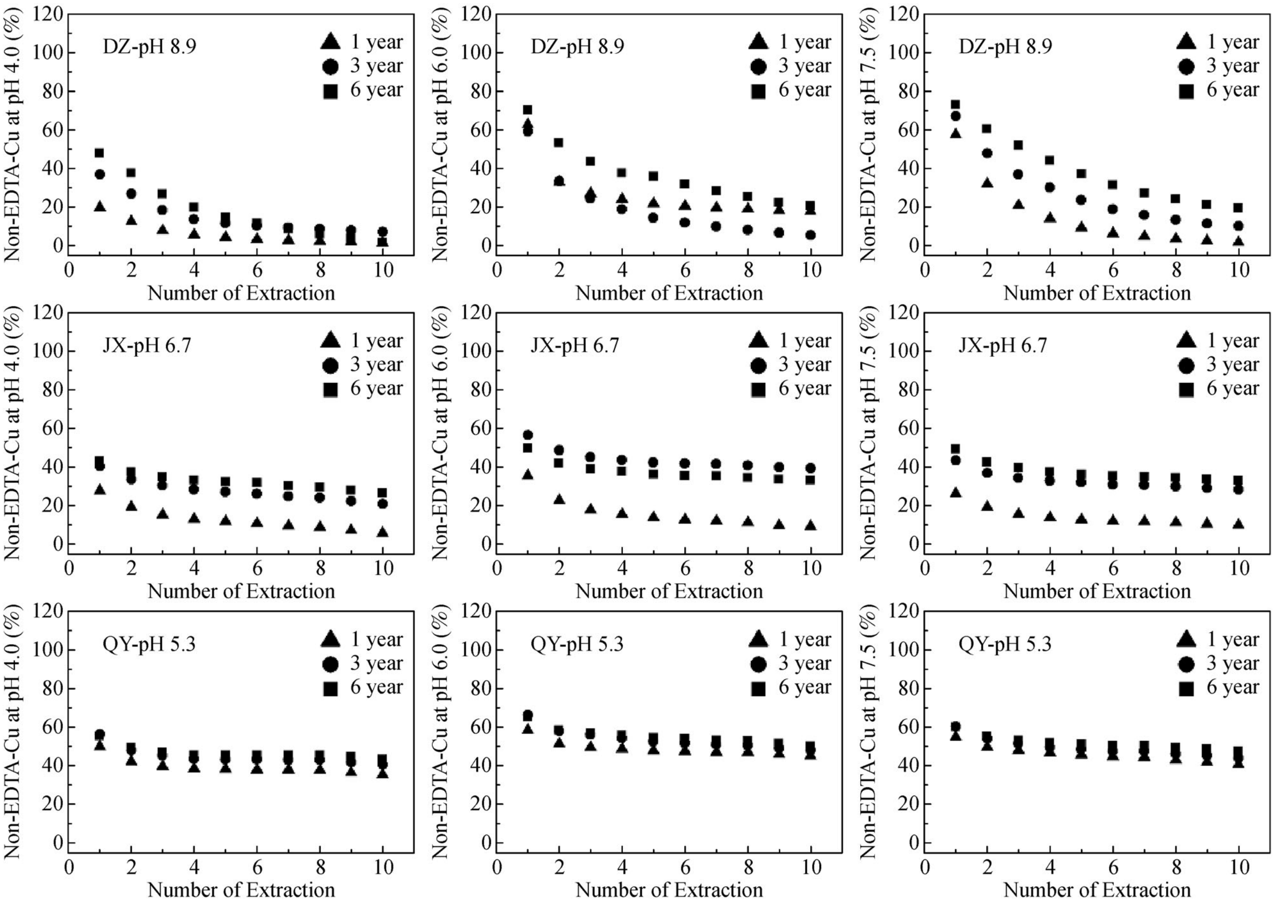

Fig. 2 Change in proportions of non-EDTA-extractable Cu (non-EDTA-Cu, %) with 1 to 10 extractions at pH 4.0, pH 6.0, and pH 7.5 to total Cu added to acidic (QY-pH 5.3), neutral (JX-pH 6.7), and alkaline (DZ-pH 8.9) soils aged for 1, 3, and 6 years

extractability of added Ni (from 21.2% to 31.1%, 27.8% on average) was lower than that of Cu (from 36.5% to 41.5%, 39.4% on average) in the first sequential extractions, although ten-EDTA-Ni (from 47.6% to 63.2%, 57.3% on average) was similar to ten-EDTA-Cu (from 52.2% to 60.2%, 56.1% on average). In neutral and alkaline soils, ten-EDTA-Ni (from 44.0% to 46.9%, 45.0% on average in neutral soil; from 13.5% to 24.4%, 18.4% on average in alkaline soil) was significantly lower than ten-EDTA-Cu (range 72.6% to 82.2%, 77.0% on average in neutral soil; 85.4% to 96.6%, 90.6% on average in alkaline soil). In addition, the effects of aging were more significant on Ni than Cu. From 1 to 6 years, the decreased extractability of Ni (18.1%, 63.2%, and 22.0%) was greater than that of Cu (6.63%, 22.5%, and 6.87%), indicating that the aging process of Ni was faster than that of Cu from 1 to 6 years, which was in agreement with the fact that the aging processes of added Ni were controlled by the micropore diffusion processes [12] and the fast aging processes of precipitation/nucleation were the predominant processes leading to decreases in isotopic exchangeability of added Cu [9].

4 Conclusions

Generally, the phytotoxicity of Cu and Ni added to field soils initially decreased quickly, then slowly with aging time. For the long-term (from 1 to 6 years) field experiment, the decrease in phytotoxicity of added Cu and Ni was only easily identified in neutral soil, while in acidic and alkaline soils there was no big difference between biological variance and aging effect on phytotoxicity of Cu and Ni. As a better indicator of effect of aging, the extractability of Cu and Ni by EDTA tended to decrease with aging time from 1 to 6 years in three different soils (acidic, neutral, and alkaline soils) at three pHs (pH 4.0, pH 6.0, and pH 7.5) of extractant. In neutral and alkaline soils, 10 sequential extractions removed more Cu than Ni, but in acidic soil this only occurred in the first extraction. In addition, the effects of aging were greater on Ni than Cu from 1 to 6 years because of the aging processes of added Ni controlled by the micropore diffusion and the aging of added Cu controlled by precipitation/nucleation.

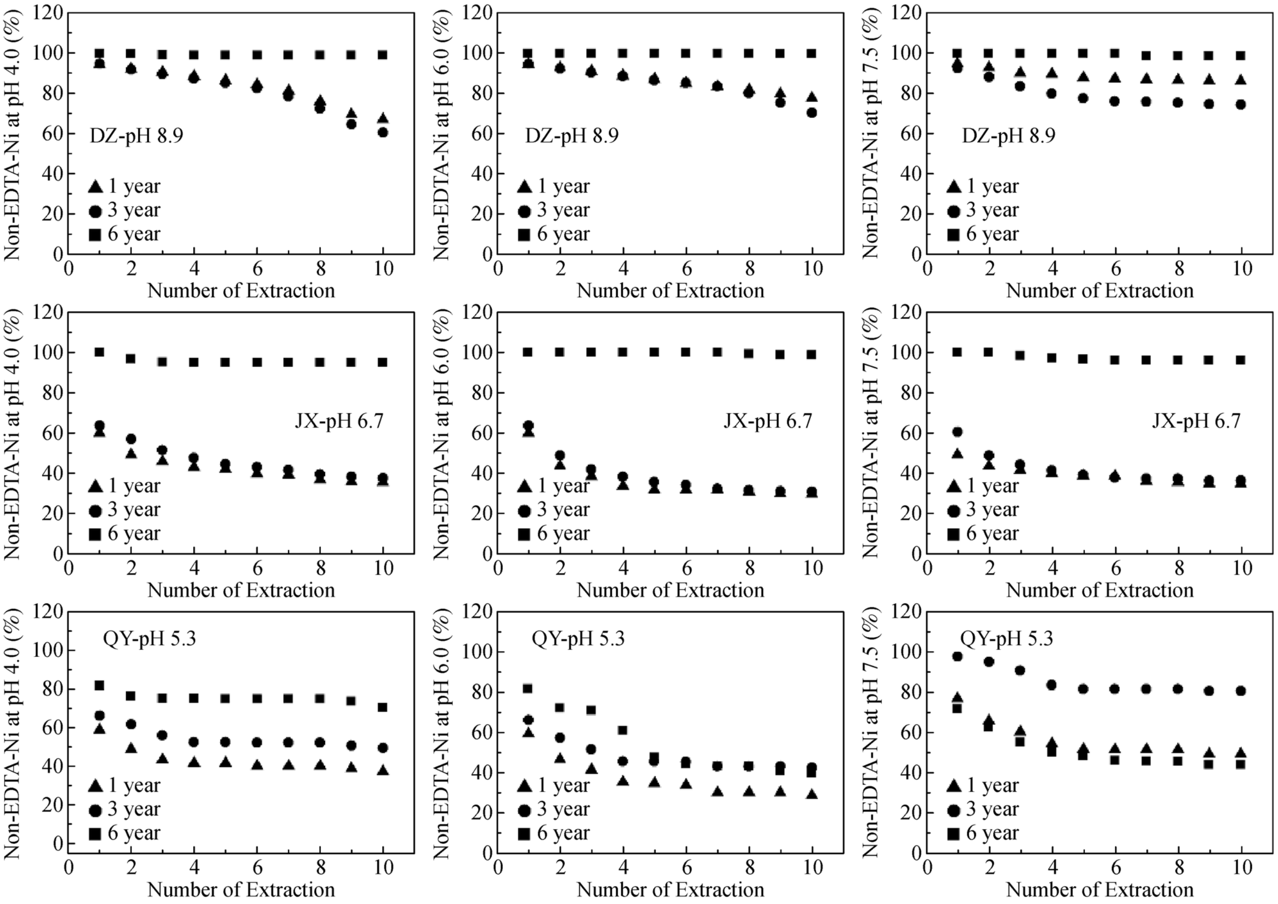

Fig. 3 Change in proportions of non-EDTA-extractable Ni (non-EDTA-Ni, %) with 1 to 10 extractions at pH 4.0, pH 6.0, and pH 7.5 to total Ni added to acidic (QY-pH 5.3), neutral (JX-pH 6.7), and alkaline (DZ-pH 8.9) soils aged 1, 3, and 6 years

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