Journal of Soils and Sediments (2020) 20:3712–3721
https://doi.org/10.1007/s11368-020-02676-2

SOILS, SEC 5 • SOIL AND LANDSCAPE ECOLOGY • RESEARCH ARTICLE

Soil accumulation and chemical fractions of Cu in a large and long-term coastal apple orchard, North China

Chuancheng Fu[1,2] • Chen Tu[2] • Haibo Zhang[3] • Yuan Li[2] • Lianzhen Li[2] • Qian Zhou[2,4] • Kirk G. Scheckel[5] • Yongming Luo[1,2,4]

Received: 16 October 2019 / Accepted: 17 May 2020 / Published online: 8 June 2020

Abstract

Purpose Coastal orchards, with greater humidity and precipitation, are favorable for fruit production, as well as mildew fungi development, thus becoming hot spots of Cu concentrations in soils due to the use of copper-based fungicides. However, little is known on the variation tendencies of Cu availability and mobility from these soils. This study aims to investigate the accumulation, spatial-temporal distribution, and chemical fractions of soil Cu in one of the largest coastal apple-producing area with over 40-year intensive cultivation in China.

Materials and methods A total of 104 orchard and 31 farmland topsoil samples were collected from Jiaodong Peninsula, Shandong Province. The total Cu concentration (T-Cu) and major element components (MnO, TiO_2, SiO_2, Fe_2O_3, and Al_2O_3) in the soil were determined by X-ray fluorescence spectroscopy. Available Cu concentration (A-Cu) was extracted with HCl or DTPA. Chemical fractionations of Cu were determined via sequential extraction method. The variation tendencies of T-Cu, A-Cu, Cu available ratio (AR), and chemical fractions with planting duration in the orchards were explored while a cokriging method was selected to predict their spatial distributions. Moreover, Pearson's correlation and multiple linear stepwise regressions were constructed to distinguish the vital factors in controlling Cu availability and mobility from these soils.

Results and discussion The results showed that long-term application of Cu-containing fungicides had increased Cu concentrations in orchard soils (85.77 mg kg^{-1}) 3.5 times higher than the background value (24.0 mg kg^{-1}) of local agricultural soils, in which 23.8% existed in the available form. Cu in the weak acid-soluble fraction (F1, 5.0 ± 3.5 %), reducible fraction (F2, 24.7 ± 6.6%), and oxidizable fraction (F3, 18.5 ± 7.8%) in orchard soils increased significantly with increasing planting durations whereas the residual fraction (F4, 51.7 ± 15.4%) exhibited a reverse trend. Total content, available content, and chemical fractions of Cu showed strong spatial heterogeneity. The availability and mobility of Cu in orchard soils were mainly controlled by total Cu content, pH, and soil organic carbon.

Conclusions Coastal orchards under warm and humid climate condition in China exhibited higher Cu input, along with acidification and rapid organic carbon turnover in the soils, eventually leading to large accumulation and high mobility of Cu in the soils.

Keywords Accumulation · Chemical fraction · Coastal orchard · Soil · Copper · Planting duration

---

Responsible editor: Claudio Bini

✉ Yongming Luo
ymluo@issas.ac.cn

[1] CAS Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

[2] CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

[3] Zhejiang Provincial Key Laboratory of Soil Contamination Bioremediation, School of Environmental and Resource Sciences, Zhejiang A & F University, Hangzhou 311300, China

[4] University of Chinese Academy of Sciences, Beijing 100049, China

[5] Center for Environmental Solutions & Emergency Response, United States Environmental Protection Agency, Cincinnati, OH 45268, USA

1 Introduction

Copper (Cu) is not only an essential nutrient for plant growth but also a hazardous heavy metal in the environment in excess concentrations (Michaud et al. 2007; Wu et al. 2010; Yang et al. 2015). Copper in most soils is derived mainly from parental rock weathering, but in some soils, anthropogenic activities may be the dominant source (Pietrzak and McPhail 2004; Ballabio et al. 2018). Since the fungicidal properties of copper were recognized two centuries ago (Fernández-Calviño et al. 2009), copper-based fungicides have been widely used in fruit orchards, vineyards, and vegetable crops to control fungal diseases (Wang et al. 2009). Long-term application of cupric fungicides has resulted in extensive Cu accumulation in the soils ranging from 1 up to 3215 mg kg^{-1} worldwide, especially when orchard age and application times increase (Fernández-Calviño et al. 2009; Mackie et al. 2012; Fu et al. 2018a). Coastal areas have marine climates, with humid air and high rainfall, which is propitious to the growing of tree fruits (Li et al. 2014). However, the greater humidity and precipitation also makes coastal areas a hot spot of Cu concentrations in soils through fungicidal application (Fernández-Calviño et al. 2009; Mackie et al. 2012).

Total Cu contents in orchard soils do not provide sufficient information to estimate its environmental impact (Vázquez et al. 2016). Indeed, Cu can be associated with various soil components that differ in their ability to retain or release it (Chopin et al. 2008). Thus, Cu availability to biota (as a nutrient or toxin) and its mobility are the most important aspects to be considered when assessing its effect on the total environment (Pietrzak and McPhail 2004). Although previous work has shown T-Cu increased remarkably in coastal orchard soils under long-term cultivation, little is known on the variation tendencies of Cu availability and mobility. The interrelationship between Cu and soil properties is always sophisticated, as soil properties are well known to have a strong influence on Cu accumulation and bioavailability in any soil (Wightwick et al. 2008; Fernández-Calviño et al. 2009). Moreover, soil characteristics such as acidity and soil organic matter (SOM) are demonstrated to change significantly among different planting durations due to intensified management in coastal orchards (Wang et al. 2009; Li et al. 2014; Fu et al. 2018b); thus, more precise details of their influence on the availability and mobility of Cu in orchard soils are warranted. Delineation of the geographic distribution of soil metals based on limited samples is necessary for better understanding the deficiencies or toxicities in plants, livestock, and humans (Wu et al. 2010; Fu et al. 2018a). At present, few studies pay attention to the spatial distribution of available and mobile fraction of Cu in coastal orchard soils, thus impeding the efficient risk management and remediation of the polluted orchard soils.

Thus, this study was conducted in a typically large and long-term coastal orchard area to further reveal the tendencies and spatial distributions of Cu accumulation and fractions. The objectives of this study were (i) to investigate the change of soil Cu concentration and partitioning in coastal orchards with different planting durations, (ii) to investigate the spatial distribution of soil Cu concentration and fractions in coastal orchards, and (iii) to understand the influence of soil properties on the availability and mobility of Cu in coastal orchard soil.

2 Materials and methods

2.1 Study area

The study area is located in Jiaodong Peninsula, Shandong Province, China (Fig. 1). Jiaodong Peninsula is adjacent to the Bohai Sea and the Yellow Sea bounded by east longitude between 119° 45′ and 122° 75′ and north latitude between 35° 50′ and 38° 85′ with a total area of 30,825 km^2. Jiaodong Peninsula is in a warm temperate zone with a marine climate, humid air, and ample sunlight throughout the year with four distinct seasons. The area receives mean annual precipitation of approximately 650–850 mm, and the mean annual temperature is 12 °C. The elevation of the study area ranges from 0 to 1132 m. Brown soil (Hapli-Udic Argosols, Chinese Soil Taxonomy) is the dominant soil type which covers 85% of the total study area (Fig. 1). Jiaodong Peninsula has a long 40-year tradition of intensive horticultural crop production and has become a main region for apple production in China (Li et al. 2014).

2.2 Soil sampling

Soil samples were collected during April and June 2014. A total of 104 soil samples were collected in the typical apple orchards with Hapli-Udic Argosols throughout the study area (Fig. 1). Moreover, 31 farmland soils were chosen as a reference and collected from typical farmlands which were adjacent to the sampled orchards. Surrounding each sampling site, five sub-samples at depth 0–20 cm over a circle of radius 10 m were taken with a stainless steel blade and a plastic scoop, then mixed thoroughly. About 1 kg soil was taken from each composite sample, stored in a polyethylene bag, and transported to the laboratory. The locations of sampling centers were recorded by a global positioning system (GPS, Garmin GPSmap 60CSx, Garmin Ltd., Olathe, USA). The planting duration of each orchard was acquired by enquiring from the orchard manager (Fig. 1).

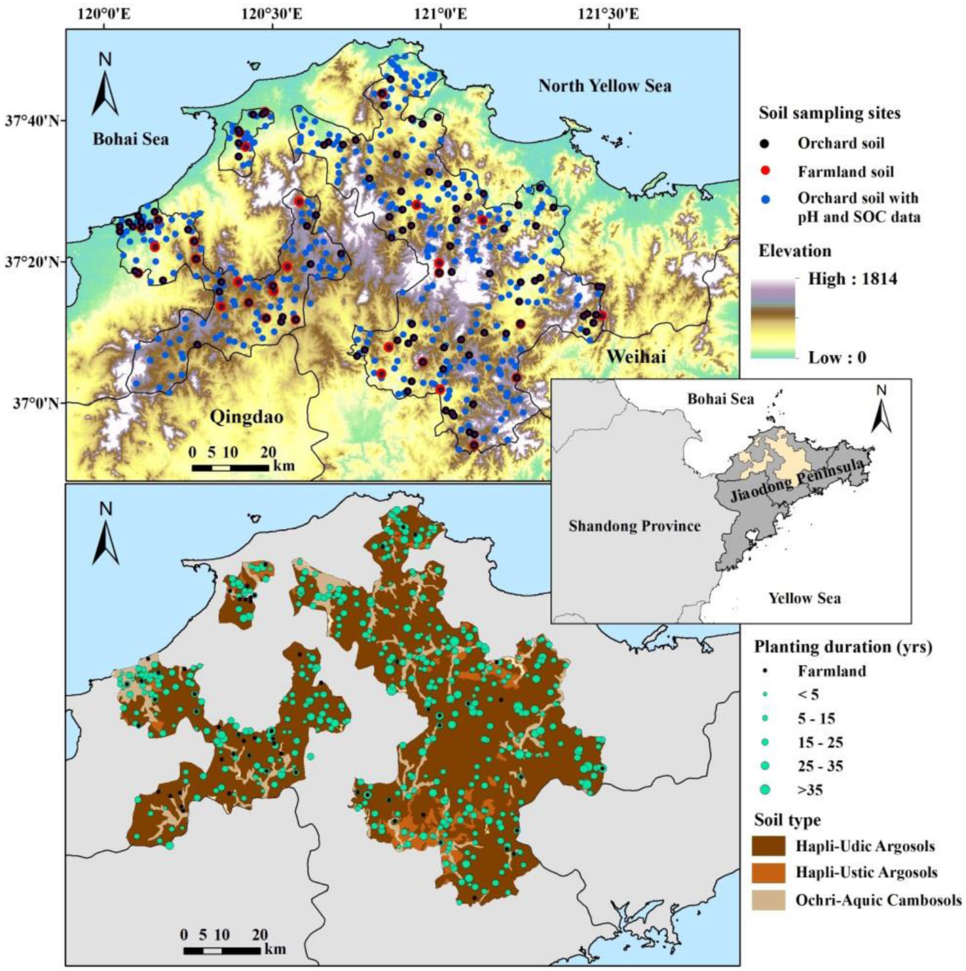

Fig. 1 The location of the study area and the distribution of soil samples

2.3 Chemical analysis

The soil samples were air-dried at ambient temperature and sieved through a 2-mm nylon mesh to remove coarse debris and plant roots. The 2-mm samples were used for the determination of soil pH and available copper (A-Cu). Portions of each sample were then ground with a ceramic pestle and mortar to pass through a 0.25-mm nylon mesh for CEC determination. Another portion of each sample was milled in an agate grinder and sieved through a 0.149-mm nylon mesh for the determination of soil total copper (T-Cu), soil organic carbon (SOC), and major elements.

The soil chemical properties were analyzed according to the routine analytical methods of agricultural chemistry in soil (Lu 1999). Briefly, soil pH value was measured in a 1:2.5 (w/v) ratio of soil to distilled water using a pH meter (Mettler Toledo Five Easy Plus FE20, Greifensee, Switzerland). Contents of SOC were determined via a CNS element analyzer (Elementar Analysensysteme Vario MACRO cube, Hanau, Germany). CEC was measured by the ammonium acetate method. Available Cu in acid soils was extracted with hydrochloric acid (0.1 mol L^{-1} HCl), whereas calcareous soils were extracted with diethylenetriamine penta-acetic acid (0.005 mol L^{-1} DTPA) (more detailed descriptions of the method can be found in LY/T 1260-1999), and then determined by inductive coupled plasma spectrometry (ICP-OES) (Optima 7000 DV, Perkin Elmer, Waltham, USA). T-Cu and major element components (MnO, TiO_2, SiO_2, Fe_2O_3, and Al_2O_3) in the soil were determined by X-ray fluorescence spectroscopy (XRF, Philips Magix Pro PW2440 instrument, Eindhoven, The Netherlands).

The optimized Community Bureau of Reference (BCR) sequential extraction method was used to determine chemical fractionations of Cu in the soil samples (Ure et al. 1993). A total of 42 representative soil samples were chosen for the BCR method according to their spatial distribution, planting duration, and soil properties. This procedure extracts metals sequentially in order: weak acid-soluble fraction (exchangeable and carbonate-associated, F1), reducible fraction (bound to Fe/Mn oxides, F2), oxidizable fraction (bound to organic matter, F3), and residual fraction (F4). The metal concentrations of the extracts were analyzed by ICP-MS (ELAN DRC II, Perkin Elmer, Waltham, USA).

Quality assurance and quality control (QA/QC) were estimated using duplicates and Certified Reference Materials (GSS-1, GBW07412a ASA-1a) approved by the National Research Center for Geoanalysis or the National Research Center for Certified Reference Materials of China. The recoveries T-Cu and A-Cu of the reference materials are 96 ± 8% ($n = 8$) and 95 ± 9% ($n = 8$), respectively. Ten percent of all soil samples were measured in duplicate, and the standard deviation of duplicate samples was within 5%.

2.4 Geostatistical interpolation of soil Cu

Cokriging with auxiliary variables can improve estimates for a less densely sampled primary variable (Wu et al. 2006). In the present study, we select a cokriging method to generate the spatial distribution of T-Cu, A-Cu, AR (Cu available ratio: [A-Cu/T-Cu]*100%), and chemical fractions by ArcGIS 10.0 (ESRI, Redlands, USA). The pH and (or) SOC were chosen as covariate(s) due to their close relationship(s) with T-Cu, A-Cu, AR, and chemical fractions (Tables 2 and 3). A total of 396 additional orchard soil samples (Fig. 1; Fu et al. 2018b) were integrated into the cokriging method to obtain detailed maps of T-Cu, A-Cu, AR, and chemical fractions. Prior to the interpolation, the Johnson transformation method was utilized to obtain normal distributions of the raw data (Fu et al. 2018a). Mean error (ME) and root mean square error (RMSE) were used to evaluate the confidence of the interpolation procedure (Fu et al. 2018a).

2.5 Statistical analysis

Pearson's coefficient in a two-tailed test was constructed to determine the relationship among T-Cu, A-Cu, AR, the percentages of Cu fractions, and different soil properties. In order to combine all geochemical information and elucidate the association between available metal pools and soil chemical characteristics, multiple linear stepwise regressions were employed. The data were log-transformed in order to normalize their distribution. All statistical analyses were carried out with the program SPSS 20.0 for Windows (SPSS, Chicago, USA).

3 Results

3.1 Accumulation and chemical fractions of Cu in the coastal orchard and farmland soils

The descriptive statistics of T-Cu, A-Cu, Cu chemical fractions, and properties (pH, SOC, CEC, Al_2O_3, SiO_2, Fe_2O_3, MnO, and TiO_2) of the orchard and farmland soil samples are shown in Table 1. The coastal soils had acidic pH with a mean value of 5.78 and 5.80 for orchard and farmland soil samples, respectively. SOC content was low for the two kinds

Table 1 Concentrations and chemical fractions of Cu in the coastal orchard and farmland soils

Type		T-Cu (mg kg^{-1})	A-Cu (mg kg^{-1})	AR (%)	F1 (mg kg^{-1})	F2 (mg kg^{-1})	F3 (mg kg^{-1})	F4 (mg kg^{-1})	pH	SOC (g kg^{-1})	CEC (cmol kg^{-1})	Al_2O_3 (%)	SiO_2 (%)	Fe_2O_3 (%)	MnO (%)	TiO_2 (%)
Orchard soil	*n*	104	104	104	35	35	35	35	104	104	104	104	104	104	104	104
	Mean	85.77	23.86	23.8	6.55	27.41	21.04	49.56	5.78	10.95	14.74	14.4	60.6	4.2	0.1	0.7
	SD	54.17	20.25	10.3	6.27	17.33	16.03	27.37	0.97	2.94	3.19	1.6	3.6	1.2	0.03	0.1
	CV	0.63	0.85	0.43	0.96	0.63	0.76	0.55	16.78	26.85	21.64	11.3	6.0	27.6	37.5	12.3
	Min.	11.60	0.09	0.3	0	4.12	2.09	13.82	3.87	4.76	7.57	11.9	47.1	2.4	0.03	0.5
	Max	307.00	101.67	51.7	27.12	61.62	56.93	145.48	8.39	21.80	24.15	20.9	66.3	10.9	0.2	1.0
Farmland soil	*n*	31	31	31	8	8	8	8	31	31	31	31	31	31	31	31
	Mean	28.71	3.24	11.4	0.53	6.20	4.67	19.51	5.80	10.64	14.34	14.3	61.8	4.1	0.1	0.7
	SD	16.00	3.17	5.9	0.65	5.10	2.75	8.09	0.8	3.07	4.38	2.2	4.3	1.6	0.04	0.2
	CV	0.56	0.98	0.5	1.23	0.82	0.59	0.41	14.39	28.85	30.54	15.2	6.9	38.3	44.4	27.3
	Min.	9.02	0.70	3.9	0	1.04	1.84	6.48	4.27	4.9	6.25	9.9	50.3	2.0	0.03	0.4
	Max	82.60	15.35	27.8	1.93	15.71	9.14	31.18	7.20	16.83	20.87	19.7	71.0	9.6	0.2	1.5

T-Cu total Cu concentration, *A-Cu* available Cu concentration, *AR* Cu available ratio, *F1* weak acid-soluble fraction, *F2* reducible fraction, *F3* oxidizable fraction, *F4* residual fraction, *n* sample number, *SD* standard deviation, *CV* coefficient of variation, *Min* minimum, *Max* maximum of coastal soils, which is in line with the low CEC value of the soils. The contents of Al_2O_3, SiO_2, Fe_2O_3, MnO, and TiO_2 had mean values of 14.4%, 60.6%, 4.2%, 0.1%, and 0.7% in the orchard soils.

Mean content of T-Cu in orchard soils was 85.77 mg kg^{-1}, approximately 3.5 times higher than the background value (24.0 mg kg^{-1}) of local agricultural soils (CNEMC 1990). Compared with the Cu thresholds (150 mg kg^{-1}, pH < 6.5) of the Chinese Soil Environmental Quality Standards (MEE 2018), the mean T-Cu in orchard soils was significantly lower ($p < 0.01$). However, 13% (14/108) of the samples were categorized as being Cu highly enriched. Farmland soils showed T-Cu concentration of 28.71 ± 16.00 (mean ± SD) mg kg^{-1}, slightly higher than the background value but significantly lower than the concentration in the orchard soils ($p < 0.01$) (CNEMC 1990). The mean content of T-Cu in the orchard soil was higher than the maximum content of T-Cu in the farmland soils, indicating that the studied orchard soils were enriched with copper and orchard use of agriculture land is likely to result in Cu accumulation. Values of A-Cu ranged between 0.09 and 101.67 mg kg^{-1} for the whole set of orchard soil samples, representing an average 23.8% of T-Cu. Values of A-Cu varied narrowly for the farmland soil (0.70–15.35 mg kg^{-1}). The mean content of A-Cu and its ratio in orchard soils were significantly higher than the corresponding content and ratio in the farmland soils. This indicated that more Cu existed in available forms in orchard soils. T-Cu in the orchard soil was partitioned into F1 (6.55 ± 6.27 mg kg^{-1}), F2 (27.41 ± 17.33 mg kg^{-1}), F3 (21.04 ± 16.33 mg kg^{-1}), and F4 (49.56 ± 27.37 mg kg^{-1}), accounting for 5.0 ± 3.5%, 24.7 ± 6.6%, 18.5 ± 7.8%, and 51.7 ± 15.4% of T-Cu, respectively. The portion of potential mobile fraction (F1 + F2 + F3) was higher in orchard soil than in farmland soil whereas the portion of residual fraction (F4) exhibited a reverse trend.

3.2 Temporal distribution of soil T-Cu, A-Cu, AR, and chemical fractions

The variations of T-Cu, A-Cu, and AR in the orchards of Jiaodong Peninsula with planting duration are displayed in Fig. 2. The T-Cu, A-Cu, and AR of the studied soils were in large dispersion for different planting durations; however, based on their mean values, linear and polynomial fit of T-Cu, A-Cu, and AR versus planting duration were deduced with high correlation coefficients (0.93, 0.87, and 0.78, respectively). T-Cu and A-Cu in the orchard soil increased significantly with the increase of planting durations for the entire chronosequence. However, samples with planting duration < 10 years showed weak increasing trends of T-Cu, A-Cu, and AR. It could be roughly estimated that soil Cu increased by 3.30 mg kg^{-1} $year^{-1}$ with increasing planting durations and about 36.1% existed in available form. Furthermore, A-Cu of the soils increased at a higher rate than T-Cu, which in return reduced the AR of the coastal orchard soils.

The partitioning of the chemical fractions (F1, F2, F3, and F4) in the orchard soils under different planting durations is shown in Fig. 3. Based on the mean values of each fraction, polynomial (F1 and F4) and linear fit (F2 and F3) versus planting duration were also deduced. F1 and F4 concentrations appeared to be on a rising trend, but after approximately 30 years of cultivation, those concentrations began to plateau or decline at a slow pace. Unlike the temporal trend of F1 and F4, concentrations of F2 and F3 elevated significantly by roughly 1.11 and 0.96 mg kg^{-1} per year, respectively. In sum, with increase in planting duration, Cu in older orchard soils shifted from dominantly stable residual forms (F4) towards more mobile fractions (F1, F2, and F3), as a result of long-term orchard management.

3.3 Spatial distribution of soil T-Cu, A-Cu, AR, and chemical fractions

The spatial distributions of soil T-Cu, A-Cu, AR, and chemical fractions (F1, F2, F3, and F4) are illustrated in Fig. 4. The cokriging method was effective in mapping the spatial distributions as the ME and RMSE were relatively low. Evident in Fig. 4, soil T-Cu, A-Cu, AR, and chemical fractions had large variations across the study areas, suggesting strong spatial heterogeneity of these soil properties. Generally, soil T-Cu, A-Cu, and AR had similar spatial patterns with high values in the central and east region and low values in the northwest region of the study area. There were some differences in

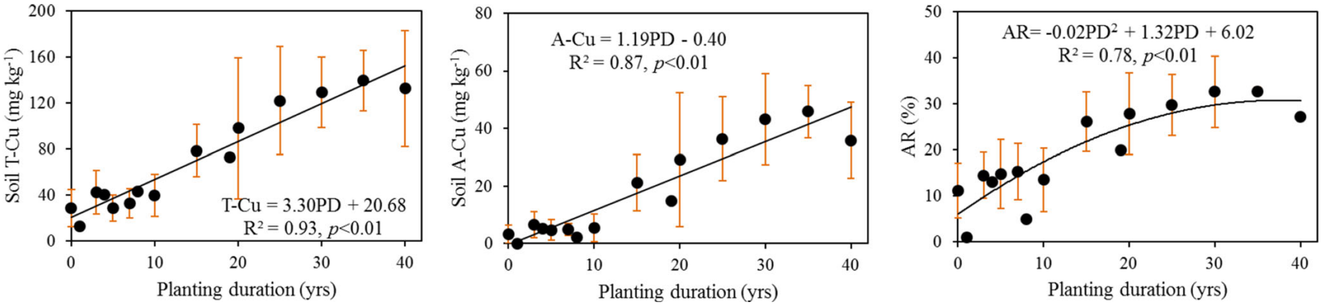

Fig. 2 Variation of T-Cu, A-Cu, and AR in the coastal orchards with planting duration. T-Cu, total Cu concentration; A-Cu, available Cu concentration; AR, Cu available ratio; PD, planting duration

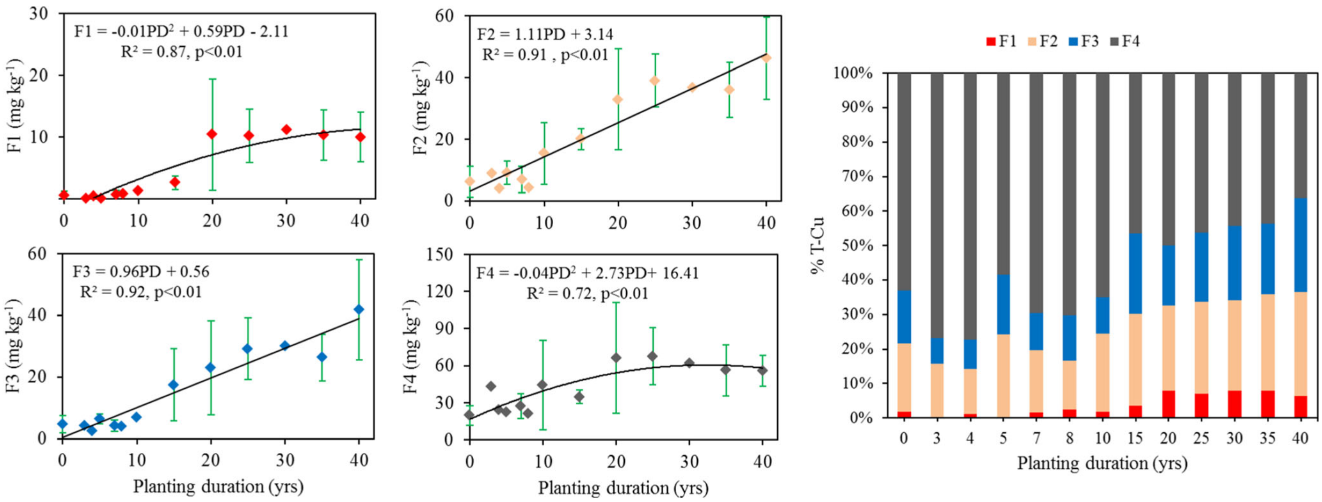

Fig. 3 Temporal distribution of Cu fractions in the coastal orchards under different planting durations. F1, weak acid-soluble fraction; F2, reducible fraction; F3, oxidizable fraction; F4, residual fraction; PD, planting duration

distribution trends between AR, T-Cu, and A-Cu concentrations. This indicates that the AR was influenced by different sets of environmental factors compared to T-Cu and A-Cu concentrations. The hot spots of T-Cu and A-Cu were mostly coincided with the old orchard having a long history of orchard management. The potentially mobile fractions (F1, F2, and F3) presented different geographic trends across the study areas. However, the same trend can also be observed in some detailed regions. The spatial distribution of F4 depicted a reverse trend with F2 and F3, but no clear distribution characteristics with F1.

3.4 The influence of soil properties on Cu accumulation and partitioning

Relationships of T-Cu, A-Cu, AR, and chemical fraction with related soil properties (pH, SOC, CEC, Al_2O_3, SiO_2, Fe_2O_3, MnO, and TiO_2) were established by determination of correlation coefficient values (Table 2). T-Cu exhibited significant positive correlation with SOC and CEC ($r = 0.303$–0.421, $p < 0.01$), indicating T-Cu increased with increasing SOC and CEC values. The negative correlation between pH and T-Cu ($r = -0.289$, $p < 0.01$) indicated that acid soils were likely to keep more Cu in the soils. Moreover, relatively poor correlations were shown between T-Cu and major element components (Al_2O_3, SiO_2, and Fe_2O_3). A-Cu was strongly correlated with T-Cu ($r = 0.927$, $p < 0.01$), indicating that A-Cu concentration increased with increase in T-Cu concentration. With regard to soil properties, pH, SOC, and CEC showed significant but less correlation with A-Cu compared with T-Cu, whereas no correlation was found between A-Cu and major element components. The potential mobile fraction (F1 + F2 + F3) showed significant and positive correlations with T-Cu, A-Cu, and AR where F4 showed a reverse correlation trend with them. Contrarily, F1, F2, and F3 significantly and negatively correlated with pH whereas F4 exhibited a reverse correlation trend.

Multiple linear stepwise regressions were conducted to identify the key soil parameters affecting the availability and mobility of Cu in the orchard soils (Table 3). All regression models are significant below 0.01 levels. Although the contents of T-Cu, A-Cu, AR, and Cu fractions could be described by the established models, the effectiveness of the models varied greatly. The variation in T-Cu was explained by pH, SOC, and Fe_2O_3 accounting for 35% of the total variance. A-Cu and AR were predicted by T-Cu and pH as evidenced by their strong correlations. With respect to the chemical fractions, T-Cu was retained in the equations except for F3. Moreover, pH was retained in the stepwise regression equations of F1, F3, and F4, whereas Fe_2O_3 was retained instead of pH for F2.

4 Discussion

4.1 Cu enrichment and its spatial-temporal distribution in orchard soils

T-Cu enrichment in the studied orchard soils is attributed to the application of Cu-based fungicide, which has been used to protect the apple trees against fungal diseases compared to field crops in the study area. Cu-based pesticides are typically applied on the foliage and can run off the leaves, thus contributing to Cu accumulation in the soil. The soil T-Cu is observed to increase roughly 3.30 mg kg^{-1} annually, which is in line with Li et al. (2005) who reported the annual Cu increase in orchard soils ranged from 2.5 to 9.0 mg kg^{-1} in Shandong Peninsula, China. Although the annual contribution of this Cu is small, its cumulative effects over years can be substantial. Our result of T-Cu content in orchard soils is comparable

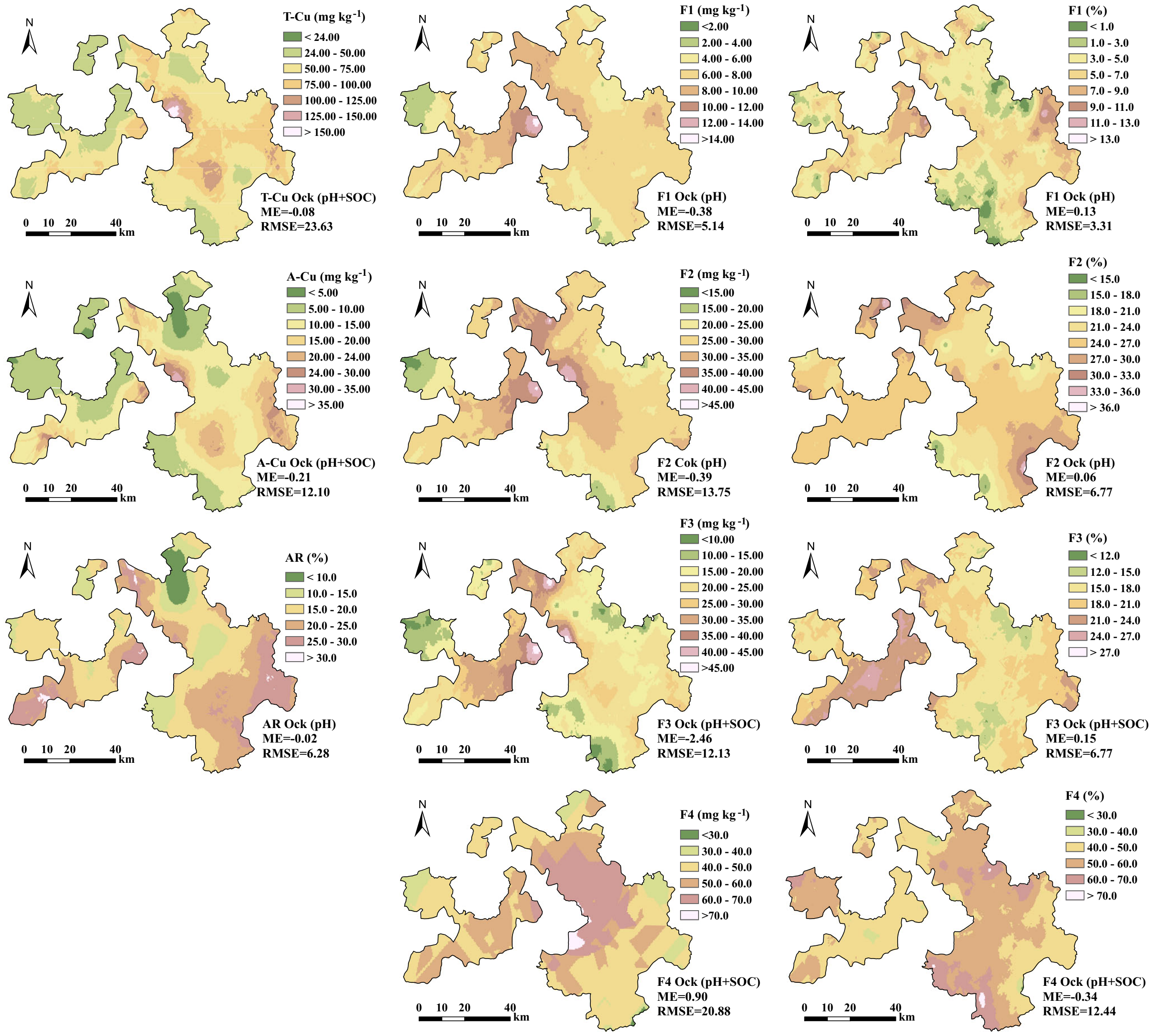

Fig. 4 Spatial distributions of Cu concentration and chemical fractions in coastal orchards soils. T-Cu, total Cu concentration; A-Cu, available Cu concentration; AR, Cu available ratio; F1, weak acid-soluble fraction; F2, reducible fraction; F3, oxidizable fraction; F4, residual fraction; SOC, soil organic carbon
ME mean error, RMSE root mean square error

with those of countries such as France (22–398 mg kg^{-1}, Chaignon et al. 2003), Australia (6–223 mg kg^{-1}, Wightwich et al. 2008), Slovenia (87–120 mg kg^{-1}, Rusjan et al. 2007), Spain (61–434 mg kg^{-1}, Fernández-Calviño et al. 2008), Portugal (25–666 mg kg^{-1}, Fernández-Calviño et al. 2009), and New Zealand (4–259 mg kg^{-1}, Morgan and Tylor 2004), but significantly lower than that of Brazil (37–3216 mg kg^{-1}, Mirlean et al. 2007). This could be associated with climatic conditions of the orchards in tropic regions of which high precipitation and temperature leads to more intensive application of Cu-based fungicides. Copper in the studied coastal apple orchard soils was significantly higher than the concentrations in the inland apple orchard soils (such as orchards in Loess Plateau; soil T-Cu, 20.09–25.94 mg kg^{-1}) in which Cu was more likely derived from parent material weathering (Chen et al. 2011). This suggests coastal orchards with greater humidity and precipitation might exhibit higher copper concentrations due to repeated Cu-based fungicide uses. These two points jointly reinforce the linkage between Cu accumulation and climate condition, thus highlighting that coastal orchards could be hotspots of soil Cu contamination due to the continuous application of Cu-containing fungicide.

Within the study area, soil Cu concentration (T-Cu, A-Cu, and chemical fractions) varied largely (Fig. 2), illustrating the heterogeneous distribution of the Cu contamination (Ruyters et al. 2013). Increasing planting duration with repeated

Table 2 Pearson's correlations between T-Cu, A-Cu, AR, and related soil properties

Item	T-Cu	A-Cu	AR	F1	F2	F3	F4
T-Cu	1			0.529**	0.533**	0.415*	− 0.599**
A-Cu	0.927**	1		0.484**	0.737**	0.576**	− 0.713**
AR	0.621**	0.807**	1	0.339*	0.856**	0.670**	− 0.774**
pH	− 0.289**	− 0.342**	− 0.437**	− 0.458**	− 0.433**	− 0.642**	0.581**
SOC	0.421**	0.339**	0.193*	0.347*	0.287	0.451**	− 0.483**
CEC	0.303**	0.232*	0.188	− 0.014	0.090	0.007	− 0.107
Al_2O_3	0.228*	0.098	− 0.151	0.067	− 0.111	− 0.142	0.056
SiO_2	− 0.283**	− 0.093	0.235*	− 0.066	0.208*	0.341*	− 0.288
Fe_2O_3	0.270**	0.100	− 0.162	0.115	− 0.244*	− 0.169	0.054
MnO	0.067	− 0.067	− 0.247**	− 0.165	− 0.210	− 0.329	0.203
TiO_2	0.134	0.069	− 0.050	0.131	0.010	0.096	− 0.139

T-Cu total Cu concentration, *A-Cu* available Cu concentration, *AR* Cu available ratio, *SOC* soil organic carbon, *CEC* cation exchange capacity, *F1* weak acid-soluble fraction, *F2* reducible fraction, *F3* oxidizable fraction, *F4* residual fraction

*Correlation is significant at the 0.05 level (2-tailed); **correlation is significant at the 0.01 level (2-tailed)

.

application of Cu-containing fungicides contributes to the disparity in T-Cu values which would be reflected on its spatial distribution (Fernández-Calviño et al. 2009). Moreover, runoff, leaching, and soil erosion also contributed to the dispersal of Cu concentrations since the orchards are mainly located on undulating hills in Jiaodong Peninsula (Mackie et al. 2012; Fu et al. 2018b). Cu released from orchard soil may reach the soils of the downhill farmland, thus leading to Cu accumulation in their soils. Moreover, sediment that originated by erosion in orchard soils could also enter the rivers which ultimately pollute the river channel. For example, a previous study reported sediment Cu enrichment in the middle stream of Jia River which runs through Jiaodong Peninsula, possibly linked to erosion of the orchard soils since industrial input was negligible (Liu et al. 2019). Thus, a relevant proportion of added Cu may have been lost from orchard soils. This could partly explain why T-Cu was not strictly monotonically increasing along the chronosequence (Fig. 2), which by the way, also implied potential risk from orchard soil pollution to the watershed.

Cu level, and especially the exogenous Cu, in soils is an important factor influencing its available and mobile pools (Fernández-Calviño et al. 2009). The exogenous Cu in orchard soils was more likely to exist in available and mobile forms, whereas reduced the proportion of the residual fraction, and consequently increasing its availability and mobility. T-Cu alone could explain 25.8–77.4% of the variability in the available (A-Cu) and mobile (F1 and F2) fractions in the present study. This could explain the similarity of spatial distributions of T-Cu, A-Cu, AR, F1, and F2. Moreover, the high correlations between A-Cu concentration and the fractions demonstrated that the potentially mobile fractions were direct sources of the A-Cu concentration in orchard soils.

4.2 The influence of soil properties on Cu accumulation and partitioning

Hapli-Udic Argosols are acidic by nature; however, soil acidification due to anthropogenic and natural acidification

Table 3 The multiple linear stepwise regression models of T-Cu, A-Cu, AR, F1, F2, F3, and F4 against soil properties

Model	*F* value	R^2_{adj}	Sig.
LogT-Cu = 1.07LogSOC − 0.09pH + 0.74LogFe_2O_3 + 0.81	19.54	0.35	0.00
LogA-Cu = 1.60Log-TCu − 0.08pH − 1.35	193.01	0.79	0.00
LogAR = 0.60LogT-Cu − 0.08pH − 0.66	35.21	0.40	0.00
LogF1 = 1.60LogT-Cu − 0.26pH − 1.22	8.46	0.41	0.00
LogF2 = 0.30LogT-Cu − 0.37LogFe_2O_3 − 1.03	11.15	0.37	0.00
LogF3 = −0.09pH + 0.65LogSOC + 1.07	15.91	0.47	0.00
LogF4 = 0.05pH − 0.15LogT-Cu − 0.42LogSOC + 2.17	11.31	0.48	0.00

Stepwise regression. Criteria: probability of *F* to enter $p \leq 0.050$, probability of *F* to remove $p \geq 0.100$

T-Cu total Cu concentration, *A-Cu* available Cu concentration, *AR* Cu available ratio, *SOC* soil organic carbon, *F1* weak acid-soluble fraction, *F2* reducible fraction, *F3* oxidizable fraction, *F4* residual fraction processes decreased the soil pH significantly (Guo et al. 2010; Li et al. 2014). T-Cu concentration and acidification were both controlled by agronomic activities in orchards. Under a long planting duration, a significant negative correlation between T-Cu and pH was expected. It had been recognized that decreased soil pH resulted in an increase in the proportion of Cu in the soluble form, altering metal speciation and availability in the soils (Alva et al. 2000; Komárek et al. 2010; Mackie et al. 2012). This supports the significant negative correlations between orchard soil pH and A-Cu and potential mobile fractions in the present study. The accumulation of SOC in the orchard soils may be explained by the constant input of organic fertilizers and fruit tree organic residual returns (Wang et al. 2009; Fu et al. 2018b). Sorption on SOM by means of complexation with humic and fulvic acids makes SOM the most important sink for Cu in soils (Strawn and Baker. 2008; Duplay et al. 2014). Cu is less mobile in organic-rich soils because it does not easily methylate or is strongly bound, forming stable complexes (Zeng et al. 2011). As directly influenced by SOC, F3 only accounts for less than 20% of T-Cu in the present study, which may be due to a relatively low SOC content. However, a worse situation could be reached if mineralization processes were dominant (Fernández-Calviño et al. 2009). Coastal orchard soils are recognized to have a rapid SOC turnover rate due to a warm and wet marine climate that favors microbial decomposition of SOC (Fu et al. 2018b). This, however, will make Cu partitioning more complex when considered simultaneously with soil acidification.

Major element components were generally considered to be important products of parent rock weathering (Lee et al. 2006; Chen et al. 2008). However, anthropogenic inputs of Cu in orchard soils may disturb the original correlation between T-Cu and major element components; thus, weak correlations were found for orchard soils. Oxides of Al and Fe have been shown to have a strong affinity for Cu (Eze et al. 2010). Week correlations of T-Cu with Al_2O_3, SiO_2, Fe_2O_3, MnO, and TiO_2 in orchard soil imply that Cu was primarily present as exchangeable ions and available forms rather than absorbed and/or co-precipitated within the crystal lattice of minerals (Chai et al. 2015). It is widely recognized that the fine soil components (e.g., clay minerals, Fe-Mn oxy-hydroxides) may well play an important role in the retention of trace elements and, consequently, in controlling the solubility and availability of contaminants (Rivera et al. 2016). However, soil constituents affecting availability are often interrelated and, thereby, the effect of these parameters is usually not straightforward (Peijnenburg and Jager 2003).

5 Conclusions

With the continuous use of Cu-based fungicides, Cu in orchard soils increased roughly up to 3.30 mg kg^{-1} per year. The exogenous Cu in orchard soils is likely to exist in available and mobile fractions with soil acidification and organic carbon enrichment, consequently increasing its availability and mobility. Total, available, and mobile fractions of Cu exhibited strong spatial heterogeneity, mainly due to the difference in amount of fungicide application, topography, dynamic of soil properties, and age of orchards. Coastal apple orchard soil in China exhibited distinct characteristics in Cu concentration and partitioning possibly influenced by planting duration, soil acidification, and rapid organic carbon turnover.

Acknowledgments The research presented was not performed by EPA and was not subject to EPA's quality system requirements. The views expressed in this article are those of the authors and do not necessarily represent the views or the policies of the U.S. Environmental Protection Agency.

Funding Information This work was financially supported by National Key R&D Programs of China (2016YFE0106400, 2018YFC1801001).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

References

Alva AK, Huang B, Paramasivam S (2000) Soil pH affects copper fractionation and phytotoxicity. Soil Sci Soc Am J 64(3):955–962

Ballabio C, Panagos P, Lugato E, Huang JH, Orgiazzi A, Jones A, Orgiazzi A, Jones A, Fernández-Ugalde O, Borrelli P, Montanarella L (2018) Copper distribution in European topsoils: an assessment based on LUCAS soil survey. Sci Total Environ 636:282–298

Chai Y, Guo J, Chai S, Cai J, Xue L, Zhang Q (2015) Source identification of eight heavy metals in grassland soils by multivariate analysis from the Baicheng-Songyuan area, Jilin Province, Northeast China. Chemosphere 134:67–75

Chaignon V, Sanchez-Neira I, Herrmann P, Jaillard B, Hinsinger P (2003) Copper bioavailability and extractability as related to chemical properties of contaminated soils from a vine-growing area. Environ Pollut 123(2):229–238

Chen T, Liu X, Zhu M, Zhao K, Wu J, Xu J, Huang P (2008) Identification of trace element sources and associated risk assessment in vegetable soils of the urban-rural transitional area of Hangzhou, China. Environ Pollut 151(1):67–78

Chen X, Zhu Y, Fu X (2011) Source and enrichment situation of heavy metals in apple orchard soils of Tianshui area, China. J Agro-Environ Sci 30(5):893–898 (in Chinese)

China National Environmental Monitoring Center (CNEMC) (1990) Chinese elemental background values for soils. Chinese Environmental Science, Beijing (in Chinese)

Chopin EIB, Marin B, Mkoungafoko R, Rigaux A, Hopgood MJ, Delannoy E, Cancès B, Laurain M (2008) Factors affecting distribution and mobility of trace elements (Cu, Pb, Zn) in a perennial grapevine (*Vitis vinifera L.*) in the Champagne region of France. Environ Pollut 156(3):1092–1098

Duplay J, Semhi K, Errais E, Imfeld G, Babcsanyi I, Perrone T (2014) Copper, zinc, lead and cadmium bioavailability and retention in vineyard soils (Rouffach, France): the impact of cultural practices. Geoderma 230:318–328

Eze PN, Udeigwe TK, Stietiya MH (2010) Distribution and potential source evaluation of heavy metals in prominent soils of Accra Plains, Ghana. Geoderma 156(3):357–362

Fernández-Calviño D, Rodríguez-Suárez JA, López-Periago E, Arias-Estévez M, Simal-Gándara J (2008) Copper content of soils and river sediments in a winegrowing area, and its distribution among soil or sediment components. Geoderma 145(1–2):91–97

Fernández-Calviño D, Nóvoa-Muñoz JC, Díaz-Raviña M, Arias-Estévez M (2009) Copper accumulation and fractionation in vineyard soils from temperate humid zone (NW Iberian Peninsula). Geoderma 153(1):119–129

Fu C, Zhang H, Tu C, Li L, Luo Y (2018a) Geostatistical interpolation of available copper in orchard soil as influenced by planting duration. Environ Sci Pollut Res 25(1):52–63

Fu C, Zhang H, Tu C, Li L, Zhou Q, Li Y, Luo Y (2018b) Spatial distribution and dynamics of soil organic carbon and total nitrogen in apple orchards in coastal regions. Acta Pedol Sin 55(4):857–867 (in Chinese)

Guo J, Liu X, Zhang Y, Shen J, Han W, Zhang W, Christie P, Goulding KWT, Vitousek PM, Zhang F (2010) Significant acidification in major Chinese croplands. Science 327(5968):1008–1010

Komárek M, Čadková E, Chrastný V, Bordas F, Bollinger JC (2010) Contamination of vineyard soils with fungicides: a review of environmental and toxicological aspects. Environ Int 36(1):138–151

Lee CS, Li X, Shi W, Cheung SC, Thornton I (2006) Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. Sci Total Environ 356(1–3):45–61

Li W, Zhang M, Shu H (2005) Distribution and fractionation of copper in soils of apple orchards. Environ Sci Pollut Res 12(3):168–172

Li L, Wu H, van Gestel CAM, Peijnenburg WJGM, Allen HE (2014) Soil acidification increases metal extractability and bioavailability in old orchard soils of Northeast Jiaodong Peninsula in China. Environ Pollut 188:144–152

Liu Q, Sheng Y, Jiang M, Zhao G, Li C (2019) Attempt of basin-scale sediment quality standard establishment for heavy metals in coastal rivers. Chemosphere 245:125596

Lu R (1999) Soil and agricultural chemical analysis methods. Chinese Agricultural Science and Technology, Beijing (In Chinese)

LY/T 1260-1999 (1999) Determination of available copper in forest soil China (in Chinese)

Mackie KA, Müller T, Kandeler E (2012) Remediation of copper in vineyards-a mini review. Environ Pollut 167:16–26

Michaud AM, Bravin MN, Galleguillos M, Hinsinger P (2007) Copper uptake and phytotoxicity as assessed in situ for durum wheat (*Triticum turgidum durum L.*) cultivated in Cu-contaminated, former vineyard soils. Plant Soil 298:99–111

Ministry of Ecology and Environment of the People’s Republic of China (MEE) (2018) Environmental quality risk control standard for soil contamination of agriculture land. GB15618–2018 (in Chinese)

Mirlean N, Roisenberg A, Chies JO (2007) Metal contamination of vineyard soils in wet subtropics (southern Brazil). Environ Pollut 149(1):10–17

Morgan RK, Taylor E (2004) Copper accumulation in vineyard soils in New Zealand. Environ Sci 1(2):139–167

Peijnenburg WJGM, Jager T (2003) Monitoring approaches to assess bioaccessibility and bioavailability of metals: matrix issues. Ecotoxicol Environ Saf 56(1):63–77

Pietrzak U, McPhail DC (2004) Copper accumulation, distribution and fractionation in vineyard soils of Victoria, Australia. Geoderma 122(2):151–166

Rivera MB, Giráldez MI, Fernández-Caliani JC (2016) Assessing the environmental availability of heavy metals in geogenically contaminated soils of the Sierra de Aracena Natural Park (SW Spain). Is there a health risk? Sci Total Environ 560:254–265

Rusjan D, Strlič M, Pucko D, Korošec-Koruza Z (2007) Copper accumulation regarding the soil characteristics in Sub-Mediterranean vineyards of Slovenia. Geoderma 141(1–2):111–118

Ruyters S, Salaets P, Oorts K, Smolders E (2013) Copper toxicity in soils under established vineyards in Europe: a survey. Sci Total Environ 443:470–477

Strawn DG, Baker LL (2008) Speciation of Cu in a contaminated agricultural soil measured by XAFS, μ-XAFS, and μ-XRF. Environ Sci Technol 42:37–42

Ure AM, Quevauviller PH, Muntau H, Griepink B (1993) Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. Int J Environ Anal Chem 51:135–151

Vázquez FAV, Cid BP, Segade SR (2016) Assessment of metal bioavailability in the vineyard soil-grapevine system using different extraction methods. Food Chem 208:199–208

Wang Q, Zhou D, Cang L (2009) Microbial and enzyme properties of apple orchard soil as affected by long-term application of copper fungicide. Soil Biol Biochem 41(7):1504–1509

Wightwick AM, Mollah MR, Partington DL, Allison G (2008) Copper fungicides residues in Australian vineyard soils. J Agr Food Chem 56:2457–2464

Wu J, Norvell W, Welch R (2006) Kriging on highly skewed data for DTPA-extractable soil Zn with auxiliary information for pH and organic carbon. Geoderma 134(1–2):187–199

Wu C, Luo Y, Zhang L (2010) Variability of copper availability in paddy fields in relation to selected soil properties in southeast China. Geoderma 156(3):200–206

Yang H, Wang, Huang Y (2015) Chemical fractions and phytoavailability of copper to rape grown in the polluted paddy soil. Int J Environ Sci Technol 12(9):2929–2938

Zeng F, Ali S, Zhang H, Ouyang Y, Qiu B, Wu F, Zhang G (2011) The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. Environ Pollut 159(1):84–91