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Distribution of Cd and Cu Fractions in Chinese Soils and Their Relationships with Soil pH: A Meta-Analysis

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Abstract: Soil contamination by potentially toxic metals (PTMs) has become a public concern in China. However, the distribution and controlling factors of soil PTM fractions remain largely unknown, limiting our ability to assess their health risks and thus to make sound controlling polices. Here, we investigate the fraction distribution of cadmium (Cd) and copper (Cu) in Chinese soils and their relationships with soil pH, based on a national meta-analysis of 163 published literatures. Exchangeable Cd in southern China accounted for 19.50 ± 14.97% of total Cd, significantly ($p < 0.01$) higher than the corresponding 13.42 ± 6.95% in northern China. Potentially available fractions constituted about 60% of total Cd at the national scale. By contrast, about half of soil Cu existed in unavailable residual fraction. Phytoavailable (i.e., exchangeable) fraction accounted for only 2.71 ± 1.65% and 2.54 ± 1.58% of total Cu in northern and southern China, respectively. Percentages of exchangeable Cd and Cu were negatively correlated ($p < 0.01$) with soil pH, while potentially available fractions increased significantly ($p < 0.05$) with soil pH. Our results provide the first national assessment of Cd and Cu fraction distribution and their responses to soil pH variations, highlighting the necessity to consider their fraction distribution and soil properties when assessing the health risks of soil PTM contamination in China.

Keywords: fraction distribution; phytoavailability; potentially toxic metals (PTMs); soil pH; Chinese soils

1. Introduction

Soil contamination by potentially toxic metals (PTMs) has drawn much attention in China during the past decades [1–3], since they may endanger human health through the transfer from soil to food [4–7]. These PTMs in soils mainly come from various anthropogenic activities, such as mining & smelting, fuel burning, fertilization, and sewage irrigation [1,3,8,9]. Preliminary estimates showed that 10–17% of Chinese croplands were polluted with PTM concentrations exceeding the Class II limits in China's soil environmental quality standard, and 13.8% of the cereals were contaminated by PTMs [3,10]. A nationwide survey, conducted between 2005 and 2013 by the Ministry of Environmental Protection (MEP) and Ministry of Land and Resources (MLR), suggested that eight PTMs (i.e., Lead (Pb), Cadmium (Cd), Mercury (Hg), Arsenic (As), Copper (Cu), Nickel (Ni), Zinc (Zn), and Chromium (Cr)) in 13.33% of the soil samples exceeded their Class II concentration limits in China's soil environmental quality standard [11,12]. Although the current status based on total concentration is still in an acceptable level, continuous pollutant loadings will increase soil PTM contamination in China [2,6].

Previous studies have reached a consensus that fraction distribution, rather than total concentration, is the governing factor for plant uptake and bioaccumulation of PTMs [13–15]. Conceptually, PTMs in soil are usually bound to organic and inorganic solid components by various processes, and thus with different phytoavailability [13,16,17]. Firstly, weakly bound exchangeable fraction is smaller in quantity, but higher in availability. Therefore, enrichments of PTMs by plant are commonly found to increase with the concentrations of exchangeable fraction [14,15]. Secondly, fractions more strongly bound to minerals and organic matter, are usually less available to plants. However, these fractions could be mobilized into available forms due to a change in environmental conditions, and therefore are considered as potentially available [18–21]. For example, studies reported that PTMs bound to carbonates were released to solution during soil acidification (i.e., soil pH decline) [22–24]. Finally, PTMs sequestered in the crystals of non-carbonate minerals are assumed as stable under conceivable natural conditions, and are usually thus considered as non-available fraction [17–19]. Therefore, understandings of fraction distribution and its influencing factors are crucial to asses the health risk of soil PTM contamination, and thus to make sound controlling policies.

Chinese soils have during the past three decades suffered from significant acidification in both agricultural and natural ecosystems, due to over N-fertilization [25] and atmospheric acidic deposition [26,27]. Understanding the relationships between PTM fraction distribution and soil pH is thus a prerequisite in order to assess the impact of soil acidification on PTM contamination in China. As a key property, soil pH has been found as the primary factor controlling the plant assimilation of PTMs [9,15,28]. Regional surveys showed that PTMs in plant tissues increased with soil pH decrease [29–31]. Furthermore, the enrichment factors of PTMs, relative to their total concentrations in soil, were negatively correlated with soil pH [32–34]. Experiments indicated that temporary soil acidification accelerated the release of soil PTMs [23,35], while increasing soil pH reduced their leaching and plant uptake [36–38]. So far, however, PTM fraction distribution and their relationships between soil pH remain unknown at the national scale. Such inadequacies constituted a knowledge gap between their total concentration and potential health risk, and hinder our ability to evaluate the influence of soil acidification on crop PTM contamination. In addition, Cd and Cu were the most polluted ones among eight investigated PTMs. They have been seen to exceed standard by the rates of 7.0% and 2.1%, respectively, in the national survey [11]. In this study, we therefore investigate the fraction distributions of Cd and Cu in Chinese soils and their relationships with soil pH, based on a national meta-analysis.

2. Materials and Methods

2.1. Data Compiliation

Fractions and total concentration of soil Cd and Cu were collected from published literatures (1990–2017) in China Knowledge Resource Integrated Database (CNKI: Beijing, China). “Soil heavy metal” was the key research word, using the term “fraction” to refine the hits. Total concentration and fractions of soil Cd and Cu as well soil pH were subsequently manually extracted from the selected literatures. Soil Cd and Cu fractions used in this study were analyzed according to the commonly used Tessier or BCR (Community Bureau of Reference) procedures [17–19]. Exchangeable, acid-soluble (i.e., bound to carbonate minerals), reducible (i.e., bound to Fe & Mn oxides), oxidizable (i.e., bound to organic matter) and residual (i.e., sequestered in non-carbonate minerals) fractions were included in our database. These fractions were sequentially extracted using solutions of salt, acetic acid, hydroxylamine hydrochloride, hydrogen peroxide, and nitric acid, respectively [17–19]. Since BCR schemes do not determine exchangeable and carbonate bound fraction separately, data for these two fractions were from the results measured using Tessier method. In this study, total concentrations of Cd and Cu were converted to mg kg^{-1} if other units were used in the original references. Five fractions were presented as their percentages of the total concentration, since most collected literatures reported them in percentage rather than absolute concentration. If original references presented the fractions in absolute concentration, their percentages were manually calculated relative the total concentration. In addition, other relevant information (e.g., site location, soil type and land use type) was collected if available in the original references. A total of 514 sites from 163 references were included in our database (Figure 1 and Supplementary Table S1).

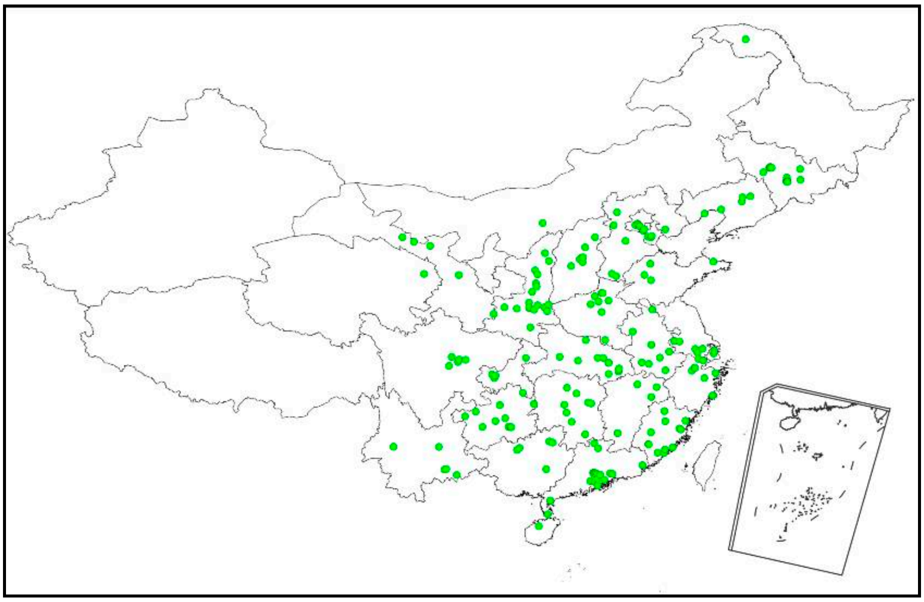

Figure 1. Geographic distribution of data used in the meta-analysis.

2.2. Data Classification

We classified the data into northern China and southern China groups, due to the distinct geographical distribution of soil pH and PTM contamination characteristics in these two regions. Data in northern China group were distributed in the northern, northeastern and northwestern China. Typical soils in these regions include cultivated loessial soils (Loessi-Orthic Primosols), fluvo-aquic soils (Ochri-Aquic Cambosols), and black soils (Udic Isohumosols). These soils are usually circumneutral or alkaline, because of lower chemical weathering. Data in southern China group covered the data from southern, southeastern and southwestern China, where red soils (Argi-Udic Ferrosols) and yellow soils (Ali-Perduic Agrosols) are the most common soil types. These soils are weakly to strongly acidic, due to long-term weathering under subtropical monsoon climate. Detailed pedogenic properties of all these soil types are described in Chinese soil taxonomy system which is basically similar to the FAO (Food and Agriculture Organization of the United Nations) system [39]. In our database, soil pH for northern China group was significantly higher ($p < 0.01$) than that for southern China group, with average pH values of 7.89 and 5.95, respectively. In addition, hills and mountains are the common landforms in southern China, with more mineral resources in this region [40]. Irrigation water contaminated by mining and smelting activities is considered to be the major source of PTMs in soil and crop [41]. By contrast, mineral resources and mining activities in northern China are much less than those in southern China [40]. According to the existing literatures, PTM contaminations in agricultural soils and crops were mainly reported in southern China [3,6,8,9].

3. Results and Discussions

3.1. Total Concentration of Cd and Cu in Chinese Soils

Total concentrations of Cd and Cu at the national and regional scales are shown in Figure 2. At the national scale, the average and median Cd concentrations were 0.86 and 0.42 mg kg^{-1}, respectively

(Figure 2a). Of the investigated soils 27% had Cd concentration lower than the Class I limit (i.e., 0.2 mg/kg) defined by the China's soil environmental quality standard [12], while 40% of them were contaminated by Cd with concentrations higher than the corresponding Class II standard (i.e., 0.6 mg kg^{-1}). These data show severer Cd contamination than the result of national survey [11]. In northern China, the average and median total soil Cd levels were 0.93 and 0.46 mg kg^{-1}, respectively. The corresponding values in southern China were 0.82 and 0.37 mg kg^{-1}, respectively. No significant difference in the total Cd concentration was found between the northern and southern China data groups (p = 0.38). Copper (Cu) concentrations were much higher than Cd, with national average and median values of 39.90 and 30.36 mg kg^{-1}, respectively (Figure 2b). This is close to the result of Niu et al. (2013), showing average and median Cu concentration of 40.5 and 26.6 mg kg^{-1}, respectively [4]. Song et al. (2014) reported a total Cu concentration of 30.67 $\pm$ 12.19 mg kg^{-1} (n = 86) in Chinese croplands [10]. In our database, Cu concentration in 61% of the soils was lower than the Class I concentration limit in Chinese soil environmental quality standard, while 6% of them were higher than the corresponding Class II standard. In addition, significantly different total Cu concentration was not observed between northern and southern China, with averages of 38.61 and 40.77 mg kg^{-1}, respectively. This Cu contamination status is basically similar to the results from national survey [11] and other meta-analysis [3,4].

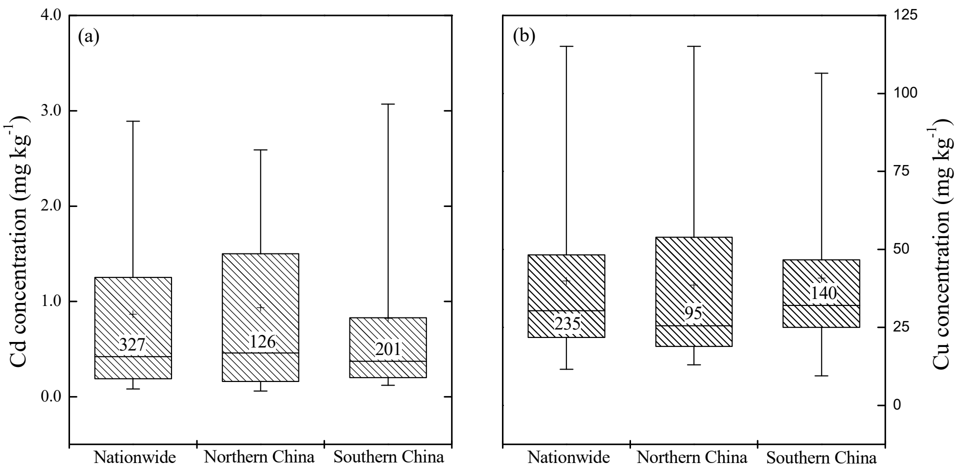

Figure 2. Distribution of total concentration of Cd (**a**) and Cu (**b**) in Chinese soils. The line and cross within the box represents the median and average value of all data, respectively; the bottom and top edges of the box represent 25 and 75 percentiles of all data, respectively; and the bottom and top bars represent 5 and 95 percentiles, respectively.

3.2. Fraction Distribution of Cd and Cu in Chinese Soils

Fraction distribution of soil Cd is shown in Figure 3a. At the national scale, exchangeable Cd accounted for 17.13 $\pm$ 13.44% of the total amount, with the 10, 50 (i.e., median) and 90 percentiles of 4.88%, 15.97% and 38.55%, respectively. This percentage range is close to the result in paddy soils in southern China [28]. Such high percentage of exchangeable Cd may account for the frequently reported Cd enrichments in plants [32,34,42], since it is considered as the most phytoavailable faction. About 60% of total Cd existed as potentially available fractions, with the average percentages of 17.13%, 18.95% and 25.72% for acid-soluble, reducible and oxidizable fraction, respectively. Totally, these four fractions took up ca. 80% of total Cd, showing its higher health risk in China and highlighting the importance to stabilize these potentially available fractions for soil Cd contamination remediation. The percentage of exchangeable Cd in northern China was 13.42 $\pm$ 6.95%, with the 10, 50 and 90 percentiles of 4.81%, 15.25% and 25.17%, respectively. The corresponding values in southern China were 19.50 $\pm$ 14.97, 5.00, 16.00, and 48.70%, respectively, which are significantly (p < 0.01) higher than those in northern China. This means that there is a higher health risk due to soil Cd contamination in southern China, though total Cd concentrations were not significantly different between northern and southern China (Figure 2a).

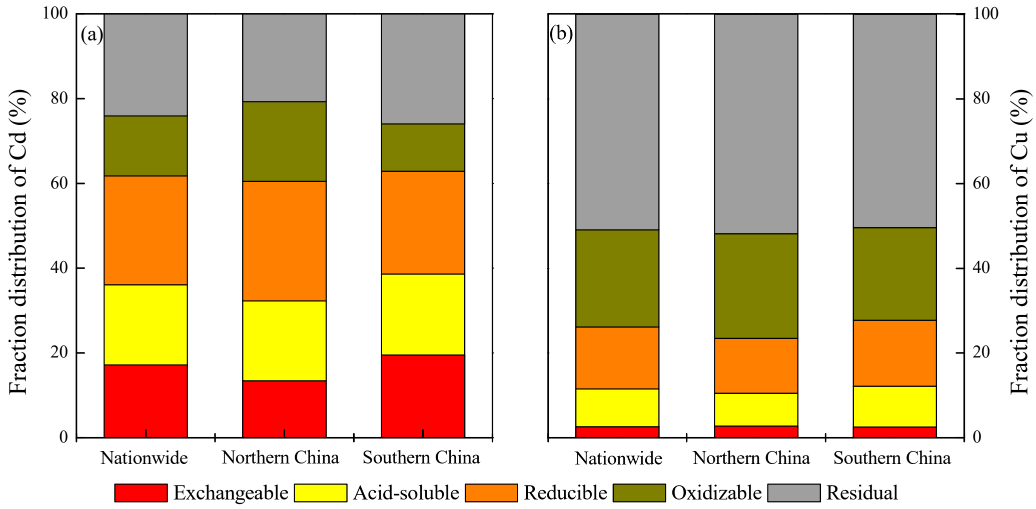

Figure 3. Averaged fraction distribution of Cd (**a**) and Cu (**b**) in Chinese soils.

As shown in Figure 3b, fraction distribution of Cu was clearly different from that of Cd. Most of soil Cu existed as non-available residual fraction, with the average and median percentages of 51.94% and 55.69%, respectively, at the national scale. Moreover, there was no significant difference (p = 0.11) in the percentage of residual Cu between northern and southern China, with average values of 51.84% and 50.40%, respectively. The exchangeable Cu fraction was only minor, with percentages of 2.61 $\pm$ 1.62%, 2.71 $\pm$ 1.65% and 2.54 $\pm$ 1.58% in nationwide, northern and southern China, respectively. Moreover, the difference in percentage exchangeable Cu between northern and southern China was not significant (p = 0.34). Acid-soluble, reducible and oxidizable fractions accounted for 18.91 $\pm$ 9.03%, 14.62 $\pm$ 11.50% and 22.92 $\pm$ 16.49% of the total Cu, respectively, at the national scale. Moreover, oxidizable Cu represented 24.71 $\pm$ 15.75% in southern China, which is significantly higher than the corresponding 21.88 $\pm$ 16.79% in northern China (p = 0.03). This is likely duo the generally higher soil organic matter content in southern China [43]. This fraction distribution pattern is consistent with the results in other literatures [20,44], indicating a lower health risk due to soil Cu contamination in China.

Our study also showed the inaccuracy in current fractionation methods of soil PTMs. For example, substantial acid-soluble fractions for both Cd and Cu were found in southern China, where soils are acidic with an average soil pH of 5.95 (Figure 3). However, significant carbonate minerals should not be expected in such acidic soils, according to the well known concepts in soil science [45,46]. This divergence is mainly due to the poor extractant selectivity, meaning that fractions other than carbonate bound can also be extracted by the dilute acetic acid [16]. In addition, strong bonds with mineral surfaces (e.g., specific adsorption) constitute important ways to retain PTMs in soil [45,46], while this fraction is not well quantified in current fractionation methods. It should be noticed that extraction procedures in BCR and Tessier methods were originally designed for sediments under reducing and circumneutral conditions [18,19]. However, soils are distinct from sediments in composition, properties, and thus in the retaining mechanisms of PTMs. This means that the same operational procedure may extract different PTM pools in soil and sediment, due to the poor selectivity of extractants. Moreover, this difference may vary with soil composition and properties. Therefore, enough attentions to these methodological artifacts should be taken when using fraction data to explain and predict the changes in soil PTMs.

3.3. Influence of Soil pH on the Fraction Distribution of PTMs

The relationships between Cd fraction percentages and soil pH are shown in Figure 4. There was a negatively correlation ($p < 0.01$) between exchangeable Cd percentage and soil pH. This means that exchangeable Cd is higher in acidic than in alkaline soils, accounting for the significant difference in exchangeable Cd percentage between northern and southern China (Figure 3a). Contrarily, the percentages of acid-soluble, reducible and oxidizable Cd increased significantly ($p < 0.05$) with soil pH increase. Such relationships indicate that there is more Cd strongly retained in alkaline soils. As shown in Figure 5, the relationships between Cu fractions and soil pH were basically similar with those for Cd fractions. However, the regression slopes for exchangeable, acid-soluble and reducible Cu were lower than the corresponding ones for Cd fractions, due to the lower percentages of these Cu fractions (Figure 3). These relationships suggest that the phytoavailability of PTMs in acidic soils is higher than those in alkaline soils, under the same total concentration. Therefore, the health risk is much higher in southern China, even though the total concentration is similar to that in northern China (Figure 2). This postulation is well supported by regional surveys showing that phytoavailability and bio-enrichment of PTMs were correlated inversely with soil pH [29,31,32,34].

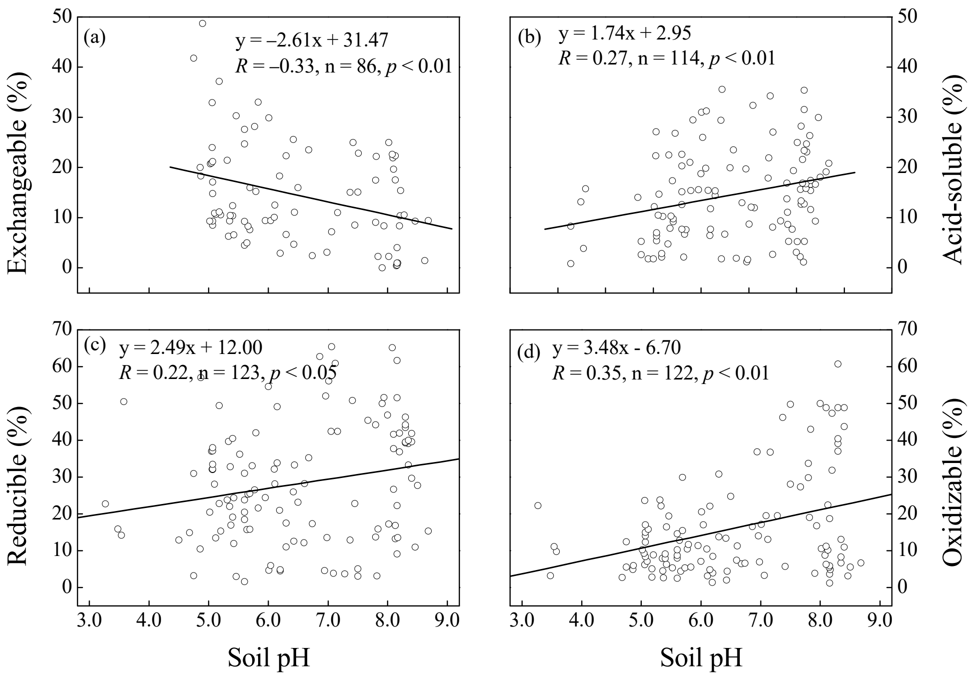

Figure 4. Spatial relationships between soil pH and Cd fractions. (**a**) exchangeable, (**b**) acid-soluble, (**c**) reducible, and (**d**) oxidizable. To remove the influence of outliers, only data between $\mu - 3\sigma$ and $\mu + 3\sigma$ were included. μ and σ are the average and standard deviation of each fraction, respectively.

These spatial relationships between PTM fractions and soil pH may be extrapolated to predict the temporal effects of soil acidification. As shown in Figures 4 and 5, the percentage of exchangeable fraction increased with soil pH decrease, meaning that soil acidification may enhance the percentage and thereby phytoavailability of PTMs. Likewise, potentially mobilizable fractions may be mobilized into available ones, since all these fractions significantly decreased with soil pH decline. Conceptually, soil acidification may cause increases in mineral dissolution, positive surface charges, and the protonation of organic matter. All these processes can promote the release of soil PTMs otherwise strongly bound to solid phases [45,47]. Laboratory experiments confirmed that soil acidification contributed significantly to the leaching of PTMs and increased their bioavailability [23,24,48]. Field experiment at Rothamsted Research station showed that 60–90% of Cd was mobilized from an acidic soil (pH = 4) during the past 100 years [22]. In China, over N-fertilization has caused significant soil acidification in major croplands, with a pH decline of between 0.13–0.8 [25]. During the similar period, soil acidification also occurred across Chinese forest and grasslands mainly due to the acidic atmospheric deposition [26,27]. According to our results, such soil acidification may have increased the phytoavailability and heath risk due to PTM contamination of crops in China.

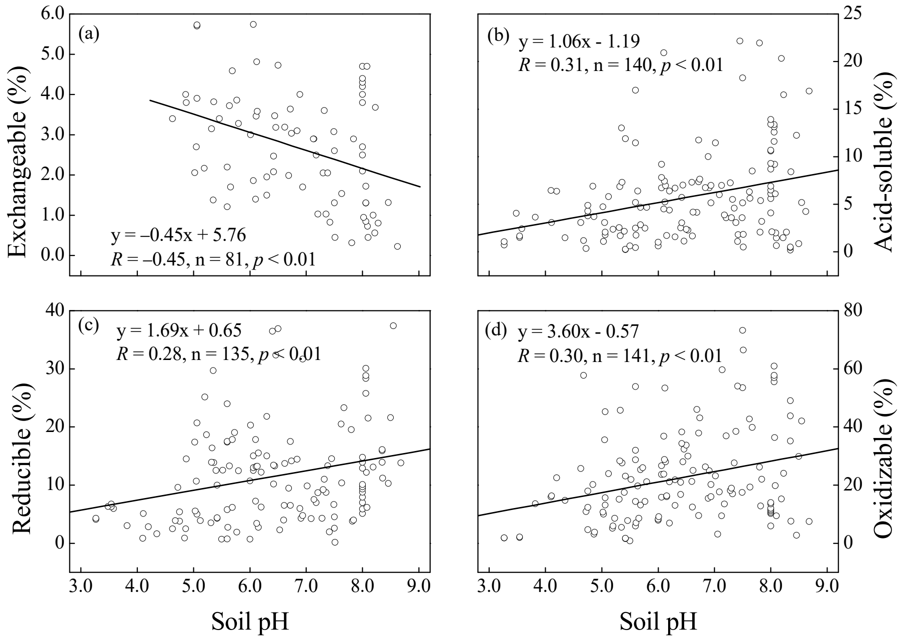

Figure 5. Spatial relationships between soil pH and Cu fractions. (**a**) exchangeable, (**b**) acid-soluble, (**c**) reducible, and (**d**) oxidizable. To remove the influence of outliers, only data between $\mu - 3\sigma$ and $\mu + 3\sigma$ were included. μ and σ are the average and standard deviation of each fraction, respectively.

3.4. Implications for the Assessment and Remediation of PTM Contamination

There are significant differences between the PTM fractions in their relative amounts and phytoavailability, which should be considered in the risk assessment and remediation of soil PTM contamination. Firstly, the available fraction (i.e., exchangeable) takes up only minor portion of the total amount, and is highly dependent on soil properties. For example, regional surveys showed that exchangeable faction of PTMs significantly increased with soil organic matter content [14,29], but decreased with soil pH [14,28]. These governing factors may account for the observed facts that soil properties controlled the bio-enrichment of PTMs [28,32,34]. Therefore, exchangeable fraction, rather than total concentration, should be used as the reasonable proxy when assessing the status and health risks of soil PTM contamination. Our results showed significant increases in exchangeable Cd and Cu percentages with soil pH decrease, suggesting a higher health risk in acidic soils under the same total PTM concentration. Therefore, PTM contamination should be controlled more strictly in southern China, due to the acidic nature of soils in this region. Current standard based on total PTM concentration may be under-protective in southern China, but over-protective in northern China. Secondly, changes in soil properties should be considered when predicting the pollution risks. Chinese soils are experiencing significant changes in soil pH [25–27] and organic carbon content [43,49]. Based on previous literatures, these changes in fundamental soil properties may cause broad impacts to the fraction distribution and phytoavailability of PTMs [24,50]. However, such influences have not been well assessed, especially at the regional and national scale. Thirdly, immobilizing the available fraction, rather than decreasing total concentration, should be the top priority to minimize the transfer of PTMs from soil to the food chain. Studies showed that increasing soil pH, by addition of lime or biochar to acid soils, significantly reduced the bioaccumulation of PTMs [36–38,51]. Although hyper-accumulating plants help to reduce the concentration of PTMs [52,53], other fractions may replenish the available fraction due to the essential control of soil properties (e.g., soil pH and organic matter).

4. Conclusions

In our database, the median values of soil Cd and Cu concentration were 0.42 and 30.36 mg/kg, respectively, without significant difference between northern and southern China. Exchangeable fraction accounted for 19.50 ± 14.97% of total Cd in southern China, which is significantly ($p < 0.01$) higher than the corresponding 13.42 ± 6.95% in northern China. About 80% of soil Cd existed in exchangeable, acid-soluble, reducible, and oxidizable factions, indicating its high phytoavailability and transfer potential from soil to plant, especially in southern China where soils are usually acidic. By contrast, unavailable residual fractions constituted about half of the total Cu. There were only 2.71 ± 1.65% and 2.54 ± 1.58% of total Cu distributed in the exchangeable pool, in northern and southern China, respectively. This fraction distribution of soil Cu suggests a lower health risk, compared with that predicted based on total Cu concentration. Fraction distribution of Cd and Cu were significantly controlled by soil pH. Percentages of exchangeable fraction increased ($p < 0.01$) with soil pH decline, while other mobilizable fractions showed clear increases in their percentages with soil pH. Our results provided the first assessment of soil Cd and Cu fraction distribution at the national scale, and further clarified the influence of soil pH on PTMs fraction distribution. These findings highlighted the necessity to consider their fraction distribution and soil properties (e.g., soil pH, and organic matter) when evaluating the health risks of soil PTM contamination in China. Moreover, these results imply that the on-going soil acidification in China may have enhanced the mobilization of PTMs, accelerating their transfer from soil to food chain.

Supplementary Materials: The following are available online at http://www.mdpi.com/2071-1050/11/2/337/s1, Table S1: A list of reference used in this meta-analysis.

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