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A Comprehensive Exploration on Pollution Characteristics and Ecological Risks of Heavy Metals in Surface Paddy Soils around a Large Copper Smelter, Southeast China

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Abstract: To assess heavy metal pollution and ecological risk, a total of 28 surface paddy soil samples were collected and analyzed around a famous copper smelter in Guixi, China. The results showed that all sites were heavily contaminated by both Cu and Cd, compared with soil background values, whose average concentrations exceeded the standard by 5.7 and 12.3 times, respectively, posing a slight ecological risk related to Cu (potential ecological risk index <40) and an extremely serious ecological risk related to Cd (potential ecological risk index >320). The risks were also demonstrated through the speciation analyses of Cu (CaCl₂-Cu 2.63%, acid-soluble Cu 8.67%, and residual Cu 74.17%, on average) and Cd (CaCl₂-Cd 47.30%, acid-soluble Cd 45.02%, and residual Cd 28.87%, on average) in the surface paddy soil, including the use of a CaCl₂ extraction procedure and the BCR (Community Bureau of Reference) sequential extraction scheme. Several soil properties (residual carbon, cation exchange capacity, and soil texture) were significantly correlated with soil Cd but made a small contribution to their variability with a poor linear fit because of external Cd input to the soil, while soil total potassium largely influenced the soil Cu species except for residual Cu. Therefore, an effective Cu pollution regulation strategy through soil potassium control is suggested for this smelter soil.

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1. Introduction

With rapid urbanization and industrial development, the heavy metal pollution of agricultural soil has been a great challenge all over the world [1–3]. A report from the Ministry of Environmental Protection of China (MEP) shows that 19.40% of the investigated cropland soil samples had pollutants exceeding the standard, and most of them were heavy metals [4]. Anthropogenic inputs, such as industrial emissions from nonferrous mining and smelting activities have been regarded as the most important sources of heavy metal pollution in China's agricultural soils in the past few decades [3,4].

Guixi Smelter is the largest modern copper smelter in China [5]. The long history of smelting has resulted in significantly increased concentrations of copper (Cu), cadmium (Cd), lead (Pb), and zinc (Zn) in the surrounding soils and nearby crops [6]. In the past 15 years, many reports have documented that the cropland soils around the smelter were seriously contaminated with Cu and Cd, posing high ecological risk related to these heavy metals, and some soils may also be polluted with Pb and Zn [7–9]. Subsequently, some pollution control and remediation measures have been put in place for the cropland soils near Guixi Smelter [8], e.g., (a) decreasing emissions of heavy metal elements through improving smelting processes [6], (b) optimizing fertilization [8,9], and (c) the in situ

passivation of soil heavy metals by application of alkaline materials [9]. These measures are mainly to reduce the external input of heavy metals and to change their mobility in soil to achieve the safe utilization of farmland soil [10].

Currently, using various extraction schemes (e.g., CaCl_2 extraction procedure, BCR sequential extraction scheme, and Tessier sequential extraction scheme) to evaluate the mobility and availability of heavy metals in soils is a major improvement over only evaluating the level of heavy metal content [11–13]. In addition, when evaluating the risk of heavy metal pollution in soil of agricultural land, the influence of soil properties on its availability is often ignored [14,15], in general, the availability of heavy metals in soil have been demonstrated to be associated with soil properties, including the pH [15], soil organic carbon content (SOC) [16], cation exchange capacity (CEC) [17], soil mechanical composition [18], and soil nutrients (e.g., nitrogen, phosphorus and potassium) [19]. However, no correlations between the soil properties and heavy metal contents were observed in agricultural soil in the northeast part of Tadla plain (Morocco) due to the influence of anthropogenic sources [14].

Thus, with a comprehensive investigation and analysis of paddy soils around the smelter, the objectives of this study were to (1) characterize the contamination status and ecological risk level after some pollution control; (2) reveal the characteristics of heavy metal species in the smelter-impacted paddy soil; and (3) explore the relationship between heavy metal species and soil properties in the study area, suggesting some sustainable and effective measures for the current safe soil use or soil remediation in China.

2. Materials and Methods

2.1. Study Area

Guixi Smelter, the largest porphyry copper mine smelter in China, lies to the north of the Xinjiang River in Guixi city, Southeast China, and all sampling sites were located on both sides of the Xinjiang River around the smelter (Figure 1). This area has a subtropical monsoon humid climate, and the soil parent material is derived from cretaceous red sandstone. The mean annual temperature is $18.2\text{ }^{\circ}\text{C}$, average annual precipitation is 1836.2 mm, and the average annual wind speed is $2.1\text{ m}\cdot\text{s}^{-1}$. For decades, almost 260 ha of paddy fields around the smelter have been contaminated by heavy metals through atmospheric deposition and wastewater discharge from smelting activities [6,7,10].

2.2. Soil Sampling and Analysis

According to the distribution of rice fields around the smelter, a total of 28 surface soil samples were collected (to a depth of 20 cm) in July 2018 after the early-rice harvest; the nearest sampling site to the smelter was 0.89 km, and the farthest sampling site from the smelter was 9.6 km (Figure 1). Each sample was a mixture of samples taken from five different directions in the same rice field, all samples were air dried and crushed, after which visible roots were removed, and then the soil samples were passed through a 2-mm sieve and stored for subsequent analyses [20].

Concentrations of soil heavy metals (Cu, Cd, Pb, Zn, Cr, and Ni) were determined using an inductively coupled plasma mass spectrometry method (ICP-MS, X2, Thermo Fisher, USA) with HNO_3 -HF- HClO_3 digestion as pretreatment [21]. Determination of soil physicochemical properties followed the methods recommended by Lu (2000) [22]. The total SOC of each sample was determined using oxidation method of potassium dichromate combined with concentrated sulfuric acid, soil pH was determined electrometrically using a pH electrode, soil total nitrogen (TN) was determined using Kjeldahl method with an automatic Kjeldahl azotometer (K9860, Hanon, Shandong province, China), soil available nitrogen (AN) was determined using alkali-hydrolyzed diffusion method, soil total phosphorus (TP) was determined using H_2SO_4 - HClO_4 digestion-phosphomolybdate blue spectrophotometry (UV/VIS-4802, UNICO, Shanghai, China), soil available phosphorus (AP) was measured using NH_4F -HCl extraction-phosphomolybdate blue spectrophotometry (UV/VIS-4802, UNICO, Shanghai, China), soil total potassium (TK) was measured

using NaOH-melting-flame photometric method (FP6431, Shanghai, China), soil available potassium (AK) was determined using NH_4OAc -extraciton-flame photometric method (FP6431, Shanghai, China), Cation exchange capacity (CEC) was measured using 1 M NH_4OAc exchange method, and soil particle size distribution was measured using the pipette method. Soil humus fractions, including humic acid, fulvic acid, and residual organic carbon, were determined by a modified Linfa Hill method [23]. To measure the mobility and bioavailability of heavy metals in soil, the heavy metal concentrations in soil exchangeable fraction were extracted using 0.01 M CaCl_2 and were analyzed by ICP-MS [24]; the chemical fractions of soil heavy metals were analyzed by BCR three-step sequential extraction (F1 acid-soluble, F2 reducible, F3 oxidizable, and F4 residual fraction) [13].

Figure 1. Spatial distribution of sampling sites.

2.3. Soil Heavy Metal Pollution Assessment

The geoaccumulation index method is mainly used to evaluate the pollution level of heavy metals. The calculation formula is as follows [25]:

$$I_{geo} = \log_2 \left(\frac{C_i}{1.5 \times B_i} \right) \quad (1)$$

where I_{geo} is the geoaccumulation index of heavy metal i ; C_i represents the measured value of heavy metal i ; B_i represents the soil background value of heavy metal i in Guixi city; and 1.5 is the correction coefficient. The classification standard is shown in Supplementary Material, Table S1 [26].

The potential ecological risk index method is used to evaluate the potential ecological risk of soil heavy metal pollution. The calculation formula is as follows [27]:

$$E_i = T_i \times \frac{C_i}{B_i} \quad (2)$$

where E_i is the individual potential ecological risk index of heavy metal i ; C_i represents the measured value of heavy metal i ; B_i represents the soil background value of heavy metal i in Guixi city; T_i is the toxic response factor of heavy metal i ($T_{Cu} = 5$, $T_{Cd} = 30$, $T_{Pb} = 5$, $T_{Zn} = 1$, $T_{Cr} = 2$, $T_{Ni} = 5$) [27]; and RI is the comprehensive potential ecological risk index. The classification standard is shown in Table S2 [28].

2.4. Statistical Analysis

Pearson's tests were used to determine whether the soil pH, soil humus fraction, SOC and soil texture were significantly correlated with the soil heavy metals and their chemical fractions. All these above statistical analyses were performed using Statistical Package for Social Sciences (SPSS) software [29,30]. A linear regression was used to determine the relative effect of each correlated predictor variable from Pearson's tests based on the coefficient of determination (R^2), which was performed in Origin 8.5 (Origin Lab Corporation, Northampton, MA, USA).

3. Results

3.1. Characteristics of Heavy Metal Pollution

The soil pH values of all sites were less than 7.0, with a mean value of 5.2, and 85.7% of the sites had pH values less than 5.5 with a CV of 0.08 (Table S3). The average total Cu and Cd contents were higher than the risk-screening values for soil contamination of agricultural land (Cu 50 mg·kg⁻¹ and Cd 0.3~0.4 mg·kg⁻¹ in GB 15618-2018) issued by the State Environmental Protection Administration of China, and the average concentrations of Cu, Cd, Pb, and Zn in the soil exceeded the soil background value [31] by 5.7, 12.3, 2.1, and 1.6 times, respectively (Table 1). Obviously, the excess Cu and Cd in the paddy soil around the copper smelter was more serious than that of the other heavy metals.

Table 1. Statistical characteristics of the heavy metal content in smelter-impacted paddy soil.

Heavy Metal	Maximum Value (mg·kg ⁻¹)	Minimum Value (mg·kg ⁻¹)	Mean (mg·kg ⁻¹)	CV	Background Value (mg·kg ⁻¹)
Cu	586.21	38.14	118.78	1.04	20.80
Cd	3.79	0.48	1.23	0.69	0.10
Cr	80.28	12.79	42.46	0.34	48.00
Pb	127.00	39.79	67.86	0.38	32.10
Zn	465.03	43.30	110.72	0.75	69.10
Ni	31.09	3.99	16.66	0.43	19.00

CV, coefficient of variation; the soil background values were referenced to Xu et al. (2015) [31].

The I_{geo} data also showed a higher pollution level of Cu and Cd in the paddy soil in the study area compared with the other heavy metals; the proportion of polluted points reached 100%, and more than 78.0% of the sites were moderately polluted by Cd (Figure 2). In addition, parts of the sites were slightly contaminated by Pb and Zn. Serious Cd pollution in the soil in the study area also resulted in a high potential ecological risk; 100% of the sites posed a heavy risk, and 39.3% of the sites reached extremely serious risk levels. Only 17.9% of the sites had a heavy potential ecological risk related to Cu pollution (Figure 3). Other heavy metals posed a very slight potential ecological risk with a <40 potential ecological risk index (Figure 3).

Figure 2. Igeo of heavy metals in smelter-impacted paddy soil. Igeo, geoaccumulation index; 1.5 IQR, 1.5 times interquartile range.

Figure 3. Potential ecological risk indices of heavy metals in smelter-impacted soil.

3.2. Speciation Analysis of Cu and Cd in Soil

Cu and Cd were the main heavy metal pollutants in the surface paddy soil around the smelter; however, they differed in bioavailability due to the different distributions of CaCl_2 -extractable Cu ($\text{CaCl}_2\text{-Cu}$) and Cd ($\text{CaCl}_2\text{-Cd}$) in the soil (Figure 4A,B). The percentage of $\text{CaCl}_2\text{-Cu}$ relative to the total Cu in the soil ($\text{CaCl}_2\text{-Cu}/\text{total Cu}$) was 0.32~17.90%, with a mean value of 2.63%, and 89.3% of the sites had <5% $\text{CaCl}_2\text{-Cu}/\text{total Cu}$ in soil (Figure 4A),

while the percentage of $\text{CaCl}_2\text{-Cd}$ relative to total Cd ($\text{CaCl}_2\text{-Cd}/\text{total Cd}$) was 4.31~87.54%, with a mean value of 47.3%, and 71.4% of the sites had >40% $\text{CaCl}_2\text{-Cd}/\text{total Cd}$ in the soil (Figure 4B).

Figure 4. The percentage of $\text{CaCl}_2\text{-Cu}$ relative to the TCu in the soil (A) and the percentage of $\text{CaCl}_2\text{-Cd}$ relative to the TCd in the soil (B). $\text{CaCl}_2\text{-Cu}$, CaCl_2 extractable Cu; $\text{CaCl}_2\text{-Cd}$, CaCl_2 -extractable Cd; TCd, total Cd; TCu, total Cu.

Similar speciation characteristics of Cu and Cd in the soil were also observed through the BCR-based fractionation of Cu and Cd (Figure 5a,b). The percentages of the acid-soluble (F1), reducible (F2), oxidizable (F3), and residual fractions (F4) of Cd relative to the total Cd were 11.38~82.93% (an average of 45.02%), 2.54~53.55% (an average of 23.53%), 0.04~8.77% (an average of 2.57%), and 5.50~72.01% (an average of 28.87%), respectively (Figure 5a), while the proportions of F1-Cu, F2-Cu, F3-Cu, and F4-Cu relative to the total Cu were 0.66~39.86% (an average of 8.67%), 1.62~11.10% (an average of 4.27%), 3.43~39.47% (an average of 12.88%), and 18.96~93.34% (an average of 74.17%), respectively (Figure 5b). Therefore, the BCR-based Cd speciation analysis indicated that the surface smelter-impacted paddy soil had a high mobility and availability of Cd because of the largest fraction of F1-Cd; accordingly, the surface smelter-impacted paddy soil had a relatively low Cu ecological risk due to the dominant F4-Cu fraction in the Cu species (Figure 5a,b).

3.3. Relationships of Cu and Cd Species with Soil Properties

Pearson's correlation analyses (Table S4) revealed that $\text{CaCl}_2\text{-Cu}$ was significantly correlated with TCu, F1-Cu, and F3-Cu, and the corresponding adjusted coefficients of determination (R^2) of the linear equation between them were 0.42, 0.40, and 0.40, respectively (Figure S1). $\text{CaCl}_2\text{-Cd}$ was significantly correlated with TCd, F1-Cd, F2-Cd, and F3-Cd (Table S4), and the corresponding R^2 values of the linear fitting equation were 0.73, 0.53, 0.42, and 0.15 (Figure S2). The R^2 increased to 0.67 through the establishment of a stepwise regression equation based on the three BCR-based Cd fractions (F1-Cd and F2-Cd, entered; F3-Cd, excluded), suggesting a strong linear relationship between the CaCl_2 extractable Cd and the BCR-based Cd fraction in the soil in the study area. No obvious correlation between Cu and Cd in the soil in the study area was observed, regardless of the Cu and Cd species (Table S4).

Figure 5. The percentage of BCR-based fractionation of Cd relative to the TCd in the soil (a) and the percentage of BCR-based fractionation of Cu relative to the TCu in the soil (b). F1, acid-soluble; F2, reducible; F3, oxidizable; F4, residual fraction; TCd, total Cd; TCu, total Cu.

Among the soil chemical properties, the soil pH was poorly correlated with all Cu and Cd species, while the residual organic carbon (Res-C) in SOC was significantly positively correlated with F2-Cd, and the soil CEC was significantly correlated with F2-Cd, F3-Cd, and F4-Cd (Table S5), but the goodness of fit of the linear equations between them was poor (Table 2). The soil TK was significantly negatively correlated with TCu, CaCl₂-Cu, F1-Cu, F2-Cu, and F3-Cu (Table S5), and the corresponding R^2 values of the linear equation between TK and each Cu species were 0.57, 0.33, 0.48, 0.29, and 0.63 (Table 2), suggesting that TK had a strong influence on soil Cu variability, especially on oxidizable Cu (F3-Cu) (Table 2).

Table 2. Relationship between Cu and Cd species with soil chemical properties.

Dependent Variable	Independent Variable	Linear Regression Model	Adjusted R^2	p Value (F-Test)
TCd	SOC	$TCd = 0.11 \times SOC - 0.04$	0.14	0.029 *
	ResC	$TCd = 0.12 \times ResC + 0.32$	0.16	0.019 *
	SOC	$F2Cd = 0.01 \times SOC - 0.03$	0.13	0.034 *
F2Cd	ResC	$F2Cd = 0.01 \times ResC - 0.00$	0.17	0.018 *
	CEC	$F2Cd = 0.02 \times CEC - 0.03$	0.29	0.002 **
F3Cd	CEC	$F3Cd = 0.001 \times CEC + 0.00$	0.14	0.028 *
F4Cd	CEC	$F4Cd = 0.01 \times CEC + 0.01$	0.29	0.002 **
TCu	TK	$TCu = -14.62 \times TK + 427.10$	0.57	0.000 **
CaCl ₂ Cu	TK	$CaCl_2Cu = -1.26 \times TK + 31.66$	0.33	0.001 **
F1Cu	TK	$F1Cu = -1.41 \times TK + 36.43$	0.48	0.000 **
F2Cu	TK	$F2Cu = -0.77 \times TK + 20.17$	0.29	0.002 **
F3Cu	TK	$F3Cu = -1.53 \times TK + 41.54$	0.63	0.000 **

SOC, soil organic carbon; ResC, residual organic carbon; CEC, cation exchange capacity; TK, total potassium; TCd, total Cd; F2Cd, reducible Cd; F3Cd, oxidizable Cd; F4Cd, residual Cd; TCu, total Cu; CaCl₂Cu, CaCl₂ extractable Cu; F1Cu, acid-soluble Cu; F2Cu, reducible Cu; F3Cu, oxidizable Cu. * Significant at $p < 0.05$; ** significant at $p < 0.01$.

A significant linear correlation between the soil mechanical composition and different Cd species was observed through Pearson correlation analysis in which the sand content was significantly negatively correlated with TCd, F2-Cd, and F3-Cd, while both the silt and clay contents were significantly positively correlated with TCd, F2-Cd, and F3-Cd (Table S5). The linear fitting results showed that the soil mechanical composition had a low impact on soil Cd variability because of the low goodness of fit in the linear equations ($R^2 < 30\%$) (Figure S3). In addition, all soil Cu species were poorly correlated with the sand, silt and clay contents (Table S5).

4. Discussion

4.1. Pollution Characteristics and Risk Assessment

The heavy metal geoaccumulation index indicated that the pollution level was ranked as $Cd > Cu > Pb > Zn$, the heavy pollutant was Cd, and the moderate pollutant was Cu (Figure 2). All sites had serious ecological risk related to Cd in the surface smelter-impacted paddy soil (Figure 3). These results are basically consistent with the serious combined pollution of Cu and Cd that existed in the soil around this smelter [10]; by contrast, there was a large decline (43.4%) in the TCu concentration in the surface paddy soil in the study area compared to 14 years ago [7] due to the improvement in copper smelting technology and the intensification of heavy metal pollution control [8,10].

Chemical speciation analysis of the soil heavy metals indicated that the surface paddy soil in the study area had high Cd bioavailability, while stable residual Cu (F4-Cu) dominated the Cu in the soil (Figures 3 and 4). In a previous study [7], the surface paddy soil in the study area had $>80\%$ $MgCl_2$ extractable Cd, which is much higher than that in this study ($CaCl_2$ -Cd, an average of 47.27%), and the dominant Cu species were NaOAc-HOAc-extracted Cu and acidic H_2O_2 -extracted Cu with a higher bioavailability than that in this study. The reduction in Cu and Cd pollution risk may be due to the increase in pollution regulation and the improvement of the copper smelting process in Guixi Smelter over the last decade [8].

4.2. Effects of Soil Properties on Heavy Metal Species

In this study, soil TCu and BCR-based Cu species were poorly correlated with the soil TCd and BCR-based Cd fractions (Table S4), which probably resulted from the complexity of the heavy metal pollution sources, such as wastewater irrigation, atmospheric deposition, or both factors [6,10]. Generally, a negative correlation between soil pH and heavy metal mobility and bioavailability has been well documented in numerous studies [15]; however, the soil pH was very poorly correlated with the Cu species and Cd species in this work (Table S5), which can be ascribed to a small pH variation in the soil samples with a $CV < 0.1$ (Table S3). The BCR-based soil Cd species were significantly correlated with several soil properties, including res-C, CEC, clay, silt, and sand (Table S5), but these soil properties did not fit the variability of the corresponding soil Cd species well, with a low coefficient of determination of the linear fitting equation (Table 2), which may be attributed to the large effect of external Cd input (e.g., atmospheric deposition) on the bioavailability of soil Cd that offsets the impacts of those internal properties in soil, since the newly deposited Cd was presented as higher bioavailable fractions compared to those in original soils near Guixi Smelter [6]. Among these soil properties, soil TK was demonstrated to be closely associated with different species of Cu except F4-Cu and had a high goodness of fit with F3-Cu and F1-Cu (Table 2).

Of course, the phytoavailability and ecological risk of heavy metals are also related to soil types, cropping systems, and soil amendments. Giannakis et al. (2021) concluded a low environmental risk of sludge-based biosolids when utilized in the corn field, but this varied with soil type [32]. Huang et al. (2018) developed an integrated pollution evaluation method for assessing the ecological and health risks of heavy metal pollution under different anthropogenic emissions and cropping systems in peri-urban areas [33]. Although this study comprehensively investigated and evaluated the characteristics of

heavy metal pollution in the surface paddy soils surrounding the smelter, an integrated assessment of the source–soil–plant system is needed in the future research.

4.3. Implications for Sustainable Agriculture and Heavy Metal Contamination Control

With the help of the speciation analysis of Cu and Cd, we can comprehensively understand the pollution status and risk level of the paddy soils around Guixi smelter. This can help us identify potential major risks and contamination elements in the soil and take effective prevention and control measures accordingly. In addition, the main controlling factors affecting the bioavailability of heavy metals can be found through analyzing the relationship between soil properties and the speciation of heavy metals in the smelter-impacted soil, for example, soil TK was significantly negatively correlated with $\text{CaCl}_2\text{-Cu}$, acid-soluble Cu, and oxidizable Cu, which suggests an important technical path to control Cu pollution in the paddy soil; however, the internal mechanism is being further studied to provide scientific and effective recommendations for pollution regulation in sustainable use of agricultural soils.

5. Conclusions

The serious combined pollution of Cu and Cd was observed in the surface paddy soil around the smelter. There was a high ecological risk related to Cd, and the available Cd fraction accounted for >47% of TCd, while the soil Cu was dominantly reserved in stable residual species. $\text{CaCl}_2\text{-Cd}$ was effectively predicted using F1-Cd and F2-Cd, with $R^2 > 0.67$. Several soil properties were significantly correlated with soil Cd but played a small role in its variability with a poor linear fit because of external Cd input to the soil, while soil TK largely influenced the soil Cu species, except F4-Cu, and can provide an effective Cu pollution regulation strategy through soil K control in smelter-impacted soil.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/su132313359/s1>, Figure S1: Relationship between $\text{CaCl}_2\text{-Cu}$ and the other Cu species in surface paddy soil in the study area, Figure S2: Relationship between $\text{CaCl}_2\text{-Cd}$ and the other Cd species in surface paddy soil in the study area, Figure S3: Relationship between Cu and Cd species with soil mechanical composition, Table S1: Classification standard of pollution degree based on the geoaccumulation index, Table S2: Classification standard of pollution degree based on the potential ecological risk index, Table S3: Statistical characteristics of soil pH in the surface paddy soil around the smelter, Table S4: Correlation analyses (Pearson's tests) between the different chemical speciation of Cu and Cd in soil in the study area, Table S5: Correlation analyses between the different chemical speciation of Cu, Cd and soil physiochemical properties in soil in the study area.

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Abbreviations

SOC, soil organic carbon; CV, coefficient of variation; CaCl₂-Cu, CaCl₂-extractable Cu; CaCl₂-Cd, CaCl₂-extractable Cd; TCd, total Cd; TCu, total Cu; BCR, Community Bureau of Reference; F1, acid-soluble fraction; F2, reducible fraction; F3, oxidizable fraction; F4, residual fraction; HA, humic acid; FA, fulvic acid; Res-C, residual organic carbon; AP, available phosphorus; AK, available potassium; AN, available nitrogen; CEC, cation exchange capacity; TP, total phosphorus; TK, total potassium; Clay, soil clay content; Silt, soil silt content; Sand, soil sand content.

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