Available Heavy Metal Concentrations and their Influencing Factors in Cropland and Fallows of Different Age in Tropical Area

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Abstract

To explore the effects of soil properties affected by fallow ages on available heavy metal concentrations in tropical China areas, a total of 144 topsoil samples were investigated from croplands and fallows. The total and available concentrations of chromium (Cr), copper (Cu), zinc (Zn), and lead (Pb) in the soil samples were analysed. Soil characteristics (total concentrations, pH, redox potential (Eh), organic matter (OM), particulate diameter) that may affect the available heavy metals were investigated. Additionally, the relationship between soil characteristics and available heavy metals was analysed. The results showed that the pH was lower and the Eh and OM were higher in cropland with frequent cultivation when compared to fallows which were disturbed rarely by anthropogenic activities. The particulate diameter of cropland was relatively small. The concentrations of total and available heavy metals first increased and then decreased as fallows aged. The available Cr is mainly affected by its total concentration, while the concentrations of available Cu, Zn and Pb are affected by the physicochemical properties. Soil properties of fallows changed, and the concentrations of available heavy metals can be reduced, which can reduce the bioavailability, biological toxicity and environmental impact.

Keywords: potentially toxic elements, fallow duration, physicochemical properties, agricultural soil

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available or can be made available for uptake by 
(micro)organisms from either the direct surroundings 
of the organism or by ingestion of food [10]. The 
available concentration of heavy metals is restricted 
by many factors in soil [11]. For example, the available 
concentration of heavy metals increases inversely with 
\( \text{pH} \) and decreases inversely with redox potential (Eh) 
and organic matter (OM) [12-13]. By exploring available 
heavy metal concentrations in soil and their potential 
migration and transformation in soil, their potential risk 
to the ecological environment can be better evaluated. 
Such studies can also provide a scientific and effective 
basis for the remediation of heavy metal pollution in 
soil.

In recent years, the contamination of heavy metals 
in soils has attracted much attention by scholars. A 
large number of studies on heavy metals in soil have 
been carried out with respect to source analysis, 
risk assessment, remediation, spatial distribution 
and variability [14-17]. Fallowing is allowing land 
to lie undisturbed for a season or more for fertility 
restoration. Improved fallow had been proposed as 
a solution to the heavy metal pollution associated 
with fertilizer application [18]. However, research on 
particular topics should be further studied, for example, 
whether the concentrations of available heavy metals 
can be reduced as fallows aged, the effect of the fallow 
duration on available heavy metal concentrations, and 
how long is the most suitable fallow duration. Because 
of the more favourable cultivation conditions in tropical 
areas and more times of cultivation in a year, more 
formalizers and pesticides are applied, which leads to 
the accumulation of heavy metals. In addition, the 
high temperature and precipitation in tropical areas 
will affect the concentration of available heavy metals 
during the fallow period. As the largest tropical island 
in southern China, Hainan Province has a unique 
geographical location and climate, more favourable 
production conditions, a large proportion of agricultural 
land, a high utilization rate, a high anthropogenic 
disturbance, and a variety of land-use types. This 
research aimed to address the following objectives: 1) 
to evaluate the effect of fallow ages on the dynamics 
of the total and available concentrations of four heavy 
metals (Cr, Cu, Zn, Pb) in surface (0-30 cm) soil layer 
from croplands and fallows (laid fallow for 1-3 years, 
3-5 years and >5 years); 2) to determine the relationships 
between available heavy metal concentrations and 
soil characteristics (total concentrations, \( \text{pH}, \text{Eh}, \text{OM} \), 
particulate diameter). An attempt was made to provide 
a theoretical basis for protecting the environment of 
agricultural land, ensuring the safety of agricultural 
production and preventing soil pollution.

Fig. 1. The location of the study area and distribution of the sampling sites.
Materials and Methods

Study Area

The study area (18°58'-19°44'N, 110°07'-110°40'E) is located in eastern Hainan Province, China, and includes Qionghai and Dingan counties. The total area is approximately 2899 km², and the cultivated area is 452.59 km², accounting for 15.6% of the total area. The study area is classified as a tropical monsoon climate zone that is greatly affected by monsoons, with high annual precipitation and frequent typhoons. The study area has an annual temperature of 24°C and an annual average precipitation of 1997 mm, with an uneven temporal distribution where most of the precipitation falls between May and October [19]. The rocks in the area are mainly basalt, magmatic rock and granite. The topography is high in the southwest and low in the northeast. The landform mainly consists of platform, terrace and plain areas.

Lateritic soil is the main representative soil type (GB/T 17296-2009). The parent materials of the soils are complex. Ferruginous laterite has a deep layer and a high OM content. The main landscapes of the cultivated area are paddy fields, dryland, orchards, and woodlands. Early indica rice and late indica rice are grown in the area are mainly basalt, magmatic rock and granite. The topography is high in the southwest and low in the northeast. The landform mainly consists of platform, terrace and plain areas.

Sample Sources and Pretreatment

Based on the understanding of the spatial distribution of agricultural land in the study area, twelve sampling sites with more favourable agricultural production conditions, complex land-use types and management measures were selected according to the principles of typicality and representativeness, as illustrated in Fig. 1. At each sampling site, one cropland and three fallows (laid fallow for 1-3 years, 3-5 years and >5 years, respectively) were selected as sample plots. In croplands, rice has been cultivated for more than 5 years, and the planting method is based on crop rotation. In fallows, rice, peanuts and other crops were planted before croplands laid fallow. The samples were subjected to acid microwave digestion for 20 min after heating up to 200°C. After digestion and cooling, the digest solution was placed on a hot plate, heated at 120°C to near dryness with 0.5 mL of H₂O₂, and washed and dissolved with 0.02 mol of HNO₃ after cooling. Each sample was quantitatively transferred to a volumetric flask, which was then filled to 50 mL with ultrapure water.

An environmental mixed calibration standard of Cr, Cu, Pb, Zn and Cd (10 μg/mL, Agilent, Part# 5183-4688) was diluted to produce a standard solution series in stages with 5% nitric acid (Merck, Germany). A mixed internal standard stock solution of ⁶Li, ⁶⁵Zn, ⁷⁶Ge, ⁸⁹Y, ¹⁵⁵In, ¹⁵⁹Tb, and ²⁰⁹Bi (10 μg/mL, Agilent, part# 5183-4680) was diluted to 1 μg/mL with 5% nitric acid (Merck, Germany). Under optimum conditions, the standardization curves were automatically drawn by the instrument (r≥0.9999). The main operating parameters of the instrument were as follows: RF power 1550 W, cooling gas 15.0 L/min, auxiliary gas 1.0 L/min, carrier gas 1.06 L/min, oxide formation (CeO/Ce<0.5%), and doubly charged (Ce²⁺/Ce⁴⁺<2%). The isotopes used were ⁵¹Cr, ⁶⁰Zn, ⁶⁵Cu, ¹⁰⁴Cd, and ²⁰⁹Pb. The recoveries were between 85% and 125%, and the relative standard deviation was less than 5%. The heavy metal concentrations of each sample and blank samples were analysed.

A single step extraction procedure, based upon diethylenetriaminepentaaacetic (DTPA) extraction, has been utilized in this study [20]. The DTPA extraction solution consisted of 0.005 mol/L DTPA with 0.01 mol/L CaCl₂ and 0.1 mol/L triethanolamine at pH of 7.3. A mass ratio of 1:10 soil: DTPA solution was shaken for 2 h, and then the suspension was centrifuged at 4000 rpm for 20 min, filtered through a 0.2 μm
porosity cellulose nitrate filter [21]. Extracts were analysed using an ICP-MS to determine the available concentrations of Cr, Cu, Zn and Pb in the soil.

Soil pH and Eh were determined in a 1:5 (soil:water ratio, w/v) suspension with a pH meter [22]. Soil organic carbon was first measured by wet oxidation, and the values were then converted to soil OM using the transfer factor of 1.724 [23]. Soil particulate diameter was determined with a particle size analyser (Mastersizer2000, Malvern, UK) [24].

The statistical differences of selected soil physicochemical properties and heavy metal distributions were determined by one-way analysis of variance (ANOVA) and were tested by homogeneity of variance test. The test of least significant difference (LSD<5%) was used to form homogeneous groups and differentiate between treatments. Correlations between distributions of available heavy metal and total heavy metal and selected soil properties were tested using Pearson’s correlation test. All statistical analyses in this study were performed with SPSS 19.0 and Excel 2010 software. Figures were drawn using Origin 2017 and CorelDRAW X4 software.

Results and Discussion

Soil Physicochemical Characterizations

The selected soil physicochemical properties in cropland and fallows of different age are summarized in Table 1. The results showed that there were significant differences in pH, Eh and OM between cropland and fallows of different age (P<0.05), while there were no significant differences in D10, D50 and D90. The soil in the study area was slightly acidic with a pH ranging from 5.14 to 7.29. The average values of soil pH were 5.68, 5.86, 5.99 and 6.61 in cropland, 1-3 year fallow, 3-5 year fallow and >5-year fallow, respectively. The Eh of cropland and fallows of different age were 73.00-129.40, 81.30-92.60, 71.30-89.10 and 2.20-52.70 mV, respectively. The Eh of >5-year fallow was significantly lower than that of cropland, 1-3 year fallow and 3-5 year fallow, which indicated that the soil of >5-year fallow was weakly oxidizable. Soil OM decreased as fallows aged, which was contrary to pH. Overall, the particulate diameter of 1-3 year fallow was larger than that of cropland soil, 3-5 year fallow and >5-year fallow. The coefficient of variation of soil physicochemical properties is 1.34-134.90%. The variation of particulate diameter and OM is relatively large, and the variation of pH and Eh is relatively small, which indicates that the former is more likely to be affected when external conditions change. Soil physical and chemical characteristics along with microbial properties will change with different duration of fallow, and will further affect the migration and distribution of available heavy metals in soil.

Driven by economic benefits, farmers applied a large number of pesticides and fertilizers to increase crop yields, which led to the acidification of cropland and the decrease of pH. Rice is planted in croplands of the sampling site. The soil microenvironment is relatively humid, and the base cations are easily leached. As a result, H+ accumulates on the soil colloid, and the soil pH is low. Usually, Eh is negatively correlated with pH, and the Eh in cropland is higher than that in fallows, which is contrary to pH. The OM in cropland was higher than that in fallows. Anthropogenic activities such as the application of organic fertilizers make OM continuously supplemented in cropland, which is conducive to the accumulation of OM. Because of long-term tillage, the coarse particles were fragmented, and the particulate diameter of cropland was relatively small. Compared with 3-5 year fallow and >5-year fallow, the particulate diameter of 1-3 year fallow was large. Because of the low vegetation coverage in 1-3 year fallow, the fine particles of soil tend to migrate downward with precipitation and easily lose with surface runoff.

Table 1. Selected soil physicochemical properties in cropland and fallows of different age.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Item</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>OM (g/kg)</th>
<th>D10 (μm)</th>
<th>D50 (μm)</th>
<th>D90 (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cropland</td>
<td>Mean</td>
<td>5.68</td>
<td>97.57e</td>
<td>31.44b</td>
<td>4.71a</td>
<td>39.47a</td>
<td>159.84a</td>
</tr>
<tr>
<td></td>
<td>S.E.</td>
<td>0.08</td>
<td>4.88</td>
<td>4.32</td>
<td>0.58</td>
<td>7.04</td>
<td>25.44</td>
</tr>
<tr>
<td>Fallow (1-3 years)</td>
<td>Mean</td>
<td>5.86</td>
<td>86.44ab</td>
<td>19.56b</td>
<td>10.08a</td>
<td>80.50a</td>
<td>244.60a</td>
</tr>
<tr>
<td></td>
<td>S.E.</td>
<td>0.03</td>
<td>1.58</td>
<td>2.38</td>
<td>3.70</td>
<td>28.17</td>
<td>59.95</td>
</tr>
<tr>
<td>Fallow (3-5 years)</td>
<td>Mean</td>
<td>5.99</td>
<td>79.08b</td>
<td>18.69b</td>
<td>3.00a</td>
<td>28.27a</td>
<td>116.48a</td>
</tr>
<tr>
<td></td>
<td>S.E.</td>
<td>0.04</td>
<td>2.46</td>
<td>3.99</td>
<td>0.39</td>
<td>2.07</td>
<td>12.66</td>
</tr>
<tr>
<td>Fallow (&gt;5 years)</td>
<td>Mean</td>
<td>6.61</td>
<td>35.71c</td>
<td>12.73b</td>
<td>4.83c</td>
<td>38.98c</td>
<td>179.18c</td>
</tr>
<tr>
<td></td>
<td>S.E.</td>
<td>0.19</td>
<td>7.41</td>
<td>2.09</td>
<td>2.66</td>
<td>15.63</td>
<td>48.03</td>
</tr>
</tbody>
</table>

Eh = redox potential; OM = organic matter; D10, D50, D90 = 10th-50th-90th percentile of particle diameter curve; S.E. = Standard error. Within individual depths, mean values with different letters are significantly different, and those with similar letters are non-significant (LSD, p<0.05).
Total and Available Concentrations of Heavy Metals in Cropland and Fallows of Different Age

The total and available concentrations of Cr, Cu, Zn and Pb in cropland and fallows of different age were analysed. The results are shown in Fig. 2. The total concentrations of Cr, Cu, Zn and Pb in soils were 31.06-55.60, 26.67-47.18, 10.47-25.12 and 9.22-13.18 mg/kg, respectively, showing a trend of Cr>Cu>Zn>Pb. The concentration of Cr is the highest in soil laid fallow for 3-5 years and that of Cu, Zn and Pb is the highest in soil laid fallow for 1-3 years. It can be seen that the total concentration of heavy metals in short-term fallow soil was even higher than that in cropland soil, but the total concentration of heavy metals gradually decreased as fallows aged. The average concentrations of available Cr, Cu, Zn and Pb were 8.34, 17.20, 4.92 and 4.57 mg/kg, respectively, showing a trend of Cu>Cr>Zn>Pb. Among different duration of fallow, the trend of available and total heavy metals showed a notable consistency, indicating that long-term fallow can reduce the concentration of heavy metals.

Most types of pesticides and fertilizers used in agricultural production contain heavy metals [25]. Therefore, pesticides and fertilizers have become an important source of heavy metals to cropland. Studies have shown that fallow ages can affect the distribution of heavy metal concentrations, and long-term fallow of the soil can reduce the concentration of heavy metals [26]. In this study, the total and available concentrations of Cu, Zn and Pb gradually decreased in soils that has been laid fallow for more than 3 years, while the total and available concentrations of Cr in soils gradually decreased in soils that had been laid fallow for more than 5 years, which was consistent with Tang et al. [27]. However, the concentration of heavy metals in 1-3 year fallow soils is higher than that in cropland. In the study area, fallow is adjacent to cropland. Typhoons and rainstorms occur frequently. Run-off in the cropland often flows into fallow across ridges, resulting in the fallow receiving heavy metals as well. The fallow has not been managed for a long time, so the soil is compacted, and heavy metals are accumulating continuously. Because of long-term tillage, the cropland soil is relatively loose, which is conducive to the migration of heavy metals to lower soil layers. In addition, crops also absorb some of the heavy metals in soil, resulting in heavy metals in cropland soil being lower than those in 1-3 year fallow soil.

Factors Influencing Available Concentrations of Heavy Metals

Total Concentrations of Heavy Metals

Different soil components can transform heavy metals into various fractions after entering the soil. Different environmental media can make heavy metals have a different bioavailability and mobility, reflecting...
and Pb have a high correlation coefficient with pH. Correlated with soil pH, among these metals, Cu, Zn and Pb were negatively correlated with soil pH. As shown in Table 2, the available adsorption-desorption, and coordination-dissociation equilibrium [29], the available heavy metals were determined. Soil pH is an important factor affecting the charge characteristics of their available concentrations, and the correlation coefficients were 0.795 and 0.736, respectively. Total Zn and Pb showed significant positive correlation to their available concentrations. The soil physicochemical properties such as pH, Eh, OM and particulate diameter may affect the available heavy metals in soil, the lower the concentration of available heavy metals, the higher the content of fine particles and positively correlated with D10, D50 and D90, indicating that the higher the content of fine particles, the higher the available concentration of heavy metals. In addition, the available concentrations of four heavy metals were significantly and positively correlated with the total concentration, indicating that the concentration of available heavy metals was greatly affected by the total heavy metals.

**Soil Physicochemical Characteristics**

In addition to the total concentration of heavy metals, the physicochemical properties of soil also affect the available heavy metals. Soil physicochemical properties such as pH, Eh, OM and particulate diameter may affect the available heavy metals. In this paper, the correlations among pH, Eh, OM, particulate diameter and available heavy metals were examined (Table 2), and the effects of soil physicochemical properties on available heavy metals were determined. Soil pH is an important factor affecting the charge characteristics of heavy metals, such as their precipitation-dissolution, adsorption-desorption, and coordination-dissociation equilibrium [29]. As shown in Table 2, the available concentrations of Cr, Cu, Zn and Pb were negatively correlated with soil pH. Among these metals, Cu, Zn and Pb have a high correlation coefficient with pH. When the soil pH decreases, the solubility of heavy metals in the soil solution increases, and the capacity of soil to adsorb heavy metals decreases, so the available concentration of heavy metals increases with a decrease in pH. The soil in the study area was slightly acidic with an average value of 5.96. Heavy metals were prone to migration. The Eh affects the fractions of inorganic and OM in soil by changing the valence of heavy metal ions, which leads to the migration and transformation of heavy metals. Usually, an increase in Eh will lead to a decrease in pH, which will increase the available concentrations of heavy metals. The Eh of soil samples ranged from 2.2 to 129.40 mV, with a mean value of 79.30 mV, indicating that the soil in the study area was highly oxidized. The Eh was positively correlated with available concentrations of four heavy metals, of which Cu, Zn, Pb were significantly and positively correlated with Eh, which was consistent with the conclusions of Kelderman and Osman [30]. The available concentrations of Cu, Zn and Pb were significantly and positively correlated with OM. This result is because soil OM is mainly composed of biomolecules and humus (mainly humic acid and fulvic acid), which affect the available heavy metals through electrostatic adsorption, complexation and chelation [31]. Fulvic acid is strongly acidic and mobile, which can significantly promote the desorption of heavy metals in polluted soil and improve the available concentration of heavy metals, while the adsorption capacity of humic acid is high, it can significantly reduce the dissolution of heavy metals in polluted soil. D10, D50 and D90 of the soil samples ranged from 1.52 to 41.20, 13.60 to 277.00 and 61.10 to 603.00 μm, respectively. The soil was coarse in texture. Cu, Zn and Pb were significantly and positively correlated with D10, D50 and D90, indicating that the higher the content of fine particles in soil, the lower the concentration of available heavy metals. This observation is because heavy metal ions are preferentially adsorbed and immobilized in soil components with large surface areas and have a strong adsorption capacity for heavy metal ions, e.g., oxides, clay minerals and humus, which are mainly distributed in fine particles.

<table>
<thead>
<tr>
<th>Element</th>
<th>HMs</th>
<th>pH</th>
<th>Eh</th>
<th>OM</th>
<th>D10</th>
<th>D50</th>
<th>D90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.795**</td>
<td>-0.568</td>
<td>0.554</td>
<td>0.428</td>
<td>-0.094</td>
<td>0.002</td>
<td>0.048</td>
</tr>
<tr>
<td>Cu</td>
<td>0.736**</td>
<td>-0.856**</td>
<td>0.867**</td>
<td>0.813**</td>
<td>0.564*</td>
<td>0.724**</td>
<td>0.761**</td>
</tr>
<tr>
<td>Zn</td>
<td>0.574*</td>
<td>-0.782**</td>
<td>0.808**</td>
<td>0.776**</td>
<td>0.501*</td>
<td>0.606*</td>
<td>0.549*</td>
</tr>
<tr>
<td>Pb</td>
<td>0.561*</td>
<td>-0.677*</td>
<td>0.692*</td>
<td>0.697*</td>
<td>0.766**</td>
<td>0.837**</td>
<td>0.840**</td>
</tr>
</tbody>
</table>

The subscripts “t” and “a” following heavy metal symbols indicate the total concentrations and available concentrations of heavy metals, respectively. **, * Significant at P<0.01 and P<0.05, respectively.

* HMs = heavy metals; Eh = redox potential; OM = organic matter; D10, D50, D90 = 10th-50th-90th percentile of particle diameter curve.
Conclusions

The concentration of available heavy metals differed in 1-3 year fallow, 3-5 year fallow and > 5-year fallow. As fallows aged, the physicochemical properties of fallows changed and pH, Eh, OM and particulate diameter were significantly correlated with available heavy metals. The pH was negatively correlated with available heavy metals. The Eh, soil OM and particulate diameter were positively correlated with available heavy metals. Therefore, short-term fallow of the soil cannot reduce the concentration of available heavy metals, and it may take a long time (>5 years) to reduce the concentration of available heavy metals. The duration of fallow plays an important role in reducing heavy metals in soil. More appropriate fallow methods and changes in soil properties are of great significance to the protection of cropland.

Acknowledgements

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Conflict of Interest

No potential conflict of interest was reported by the authors.

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