Effect of modified pomace on copper migration via riverbank soil in southwest China

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To explore the effects of modified pomace on copper migration via the soil along rivers in northern Sichuan and Chongqing, fruit pomace (P) and ethylene diamine tetra-acetic acid (EDTA) modified P (EP) were evenly added (1% mass ratio) to the soil samples of Guanyuan (GY), Nanbu (NB), Jialing (JL), and Hechuan (HC) from the Jialing River; Mianyang (MY) and Suining (SN) from the Fu River; and Guangan (GA) and Dazhou (DZ) from the Qu River. The morphological features and migration rules of copper in different amended soils were simulated by column experiment. Results showed that the balance time of copper in each soil column was categorized as EP - amended > P - amended > original soil , and the equilibrium time of amended soil samples at different locations was JL > SN > MY > GA > DZ > NB > GY > HC . Meanwhile , the average flow rate of copper in each soil column showed a reverse trend with the balance time. Copper in exchangeable, carbonate , and iron – manganese oxide forms decrease d with the increase of vertical depth in the soil column, among which the most evident decrease sappeared in the carbonate- bonding form. The copper accumulation in different locations presented a trend of JL > SN > MY > GA > DZ > NB > GY > HC , and the copper content under the same soil showed EP - amended > P - amended > original soil. The copper proportion of the carbonate form was the highest in each soil sample, followed by the exchangeable form . T he proportion s of iron-manganese oxide and organic matter forms were relatively small. A significant correlation was observed between the cation exchange capacity and the copper content in exchangeable and carbonate forms. Moreover, total organic carbon and copper contents were negatively correlated.

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16   **ABSTRACT**

17   To explore the effects of modified pomace on copper migration via the soil along rivers in northern Sichuan and

18   Chongqing, fruit pomace (P) and ethylene diamine tetra-acetic acid (EDTA) modified P (EP) were evenly added

19   (1% mass ratio) to the soil samples of Guanyuan (GY), Nanbu (NB), Jialing (JL), and Hechuan (HC) from the

20   Jialing River; Mianyang (MY) and Suining (SN) from the Fu River; and Guangan (GA) and Dazhou (DZ) from

21   the Qu River. The morphological features and migration rules of copper in different amended soils were

22   simulated by column experiment. Results showed that the balance time of copper in each soil column was

23   categorized as EP-amended > P-amended > original soil, and the equilibrium time of amended soil samples at

24   different locations was JL > SN > MY > GA > DZ > NB > GY > HC. Meanwhile, the average flow rate of

25   copper in each soil column showed a reverse trend with the balance time. Copper in exchangeable, carbonate,

26   and iron–manganese oxide forms decreased with the increase of vertical depth in the soil column, among which

27 the most evident decreases appeared in the   carbonate-bonding form. The copper accumulation in different

28 locations presented a trend of JL > SN > MY > GA > DZ > NB > GY > HC, and the copper content under the

29 same soil showed EP-amended > P-amended > original soil. The copper proportion of the carbonate form was

30 the highest in each soil sample, followed by the exchangeable form. The proportions of iron-manganese oxide

31 and organic matter forms were relatively small. A significant correlation was observed between the cation

32 exchange capacity and the copper content in exchangeable and carbonate forms. Moreover, total organic carbon

33 and copper contents were negatively correlated.

34 **Keywords:** Copper, Modified pomace, Riverbank soil, Morphological feature, Column experiment

35 ## INTRODUCTION

36   With the continuous innovation and development of modern industries, human society has made progress.

37 However, the pollution threat to the environment has become increasingly serious (*Pérez et al., 2006*; *Tahmineh*

38 *et al., 2013*). A large number of harmful metals (i.e., Hg, Cd, Pb, Cu, Cr, and Zn) are discharged into the soil

39 environment (*Huang et al., 2007*; *Bhuiyan et al., 2010*), thus damaging the soil microbial community, altering

40 the soil chemical properties, incorporating into plants, and ultimately entering the food cycle. Among these

41 metals, the toxicity of copper pollution cannot be underestimated. Copper pollution mainly comes from nature

42 and anthropogenic activities, and it cannot be degraded in the soil. Compared with other heavy metal elements,

43 copper pollution is more common (*Xiong et al., 2010*). It not only brings great difficulties to soil remediation

44 but also contaminates bodies of water (*Fereydoun et al., 2015*), which directly or indirectly poses threats to

45 biological and human beings. In recent years, heavy metal pollution has become increasingly serious (*Zhu et al.,*

46 *2018*; *Reetu et al., 2019*). Similarly, the developing farming industry along the Jialing River, the Fu River, and

47 the Qu River in northern Sichuan and Chongqing has caused severe copper pollution in the soil (*Mohammad,*

48 *2017*; *Li et al., 2012*). Riverbank soil is the last barrier of the river from copper pollution. Therfore, studying this

49 soil is of great significance to determine the migration features and migration rules of copper in the bank soil to

50 protect the river body.

51   Studies on the application of materials for repairing copper-contaminated soil have been widely praised

52 (*Bes & Mench, 2008*; *Malandrino et al., 2011*). Mao et al. (*2019*) found that various factors, such as ash content,

53 fixed carbon content, specific surface area, oxygen–carbon ratio, and pore size distribution, affect the copper

54   adsorption capacity by wood biochar (*Wang et al., 2019*). Shen et al. (*2017*) used NaOH/KOH modified biochar

55   (prepared by lemon residue) to adsorb copper ion and found that the adsorption rate of copper was 7.28–8.40%.

56   Thus, the influence of NaOH/KOH modification on copper adsorption was not remarkable (the adsorption rate

57   was 5.04% of unmodified biochar). Other researchers used H_3BO_3 (*Shen et al., 2017*) and H_3PO_4 (*Shen & Lei,*

58   *2016*) modified lemon residue to carry out the adsorption experiment, and the copper adsorption rate reached

59   29.71% and 26.90%, respectively. Lemon pomace contains citric acid, which can neutralize NaOH/KOH, and

60   enhances the adsorption ability of biochar. Moreover,   acid-modified material can better improve the adsorption

61   ability to copper than alkaline-modified material. Ethylene diamine tetra-acetic acid (EDTA) is an organo-

62   chemical agent and chelating agent. Previous studies have shown that EDTA has a wide range of coordination

63   properties and can form stable chelates with almost all metal ions (*Yoshinobu et al., 1997*; *Radanovi et al., 2004*).

64   The removal effect of EDTA on soil heavy metals is remarkably higher than that of other surfactants (*Wasay et*

65   *al., 1998*; *Zhang et al., 2013*). EDTA can form a EDTA-Cu chelate with high stability (*Yuan et al., 2019*), which

66   is a very favorable modifier for lemon residue modification used in copper adsorption.

67   Anyue City of Sichuan province enjoys the reputation of being "the hometown of Chinese lemon" and

68   stands out in the development of the Chinese lemon industry. The lemon planting area of Anyue City was 34700

69   hm^2 in 2018. In addition, the fresh fruit output was 580000 T, which accounted for more than 80% of the total

70   area and output of the city (*Li & Zhu, 2019*). The products developed from lemon production include lemon oil,

71   lemon fermented vinegar, lemon pectin, lemon beverage, lemon fermented fruit wine, and lemon tea. A large

72   amount of waste lemon pomace residue is produced in deep processing every year (*Qin et al., 2012*; *Shen &*

73   *Shen, 2012*). The traditional treatment method of lemon pomace involves directly discarding, landfilling,   or

74   processing the product into feed, which not only wastes resources but also has a negative impact on the

75   environment (*Zhang et al., 2006*; *Li et al., 2011*; *Hao et al., 2016*; *Li & Zhu, 2019*). Lemon pomace residue

76   contains numerous functional groups that can chelate with metal ions or molecules, such as the carboxyl group,

77   hydroxyl group, thiol group, and amino group (*Parajuli et al., 2008*). Using lemon pomace as an adsorbent not

78   only realizes the comprehensive utilization of lemon pomace but also absorbs the heavy metal in the soil to

79   achieve the purpose of soil restoration.

80   As the transition zone between land and river, riverbank soil plays an important role in the adsorption and

81   retardation of pollutant migration into river water. With the long-term discharge of industrial and agricultural

82   production wastes along rivers, heavy metal pollutants in riverbank soil are accumulating, which poses a serious

83   threat to the river water (*Li et al., 2020*). In this study, lemon pomace and EDTA-modified lemon pomace were

84   used to amend a riverbank soil sample. Then, the raw soil was taken as the control. The soil column model

85   (*Christian et al., 1999*; *Papassiopi et al., 1999*; *Hu et al., 2014*; *Sun et al., 2001*) was selected to study the

86   distribution, accumulation, migration, and morphology of copper in the riverbank soil. The purpose of this study

87   was to provide reference for the protection of river basins in northern Sichuan and Chongqing and to explore the

88   benefits of fruit residual waste for the remediation of heavy-metal-contaminated soil.

MATERIALS AND METHODS

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Materials

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91   Lemon pomace (P) was collected in Anyue City, Sichuan Province, and the samping work was conducted

92   in privately-owned land from Mr. Xie Jia. The raw P was washed with deionized water several times, dried in

93   an oven at 60 °C to constant weight, crushed, and sieved through 40 mesh size. Then, it was accurately weighed

94   to 50 g into a 1-L beaker. Afterward 250 mL of absolute ethyl alcohol and 250 mL of 0.4 mol/L NaOH solution

95   were added. Then, the solution was stirred for 24 hours and washed again with deionized water to neutral,

96   centrifugal filtration. Finally, it was put it into the oven for drying, and grounded through a 60-mesh sieve. After

97   the materials were prepared, they were set aside for later use.

98   EDTA was used as the modifier to modify the lemon pomace. A Cu^{2+} solution was prepared by using

99   analytical reagent-grade $CuSO_4 \cdot 5H_2O$. EDTA (analytical reagent) and $CuSO_4 \cdot 5H_2O$ (analytical reagent) were

100   purchased from Chengdu Kelon Chemical Reagent Factory, Chengdu City, Sichuan Province, China.

101   The specific process of EDTA-modified P (EP) preparation was as follows. First, 50 g of pretreated P

102   material was accurately weighed into a 1-L beaker. Then, a 500-mL 0.5-mol/L EDTA solution was added. Next,

103   the material was stirred evenly and put it in a constant temperature oscillator at 25 °C for 12 hours. Then, it was

104   washed to neutral with deionized water and centrifugally filtered. Finally, it was left in the oven for drying and

105   grounding through a 60-mesh sieve.

106   The soil samples were collected from three rivers in Sichuan and Chongqing. The sampling points (Fig. 1)

107   from north to south were Guangyuan (GY), Nanbu (NB), Jialing (JL), and Hechuan (HC) from the Jialingjiang

108 River; Mianyang (MY) and Suining (SN) from the Fu River; and Guang'an (GA) and Dazhou (DZ) from the Qu

109 River. Down by the village and within 50 m from the riverbank, a typical area (with same vegetation type and

110 land use pattern) was selected, and 0–20 cm soil samples were collected via multi-point sampling. The soil

111 samples were mixed evenly, air-dried, and then passed through a 60-mesh sieve. The physical-chemical

112 properties of the samples are shown in Table 1.

Experimental device

114   Riverbank soil has low clay content and higher sand content with a large particle diameter. In addition, Cu^{2+}

115 migrates faster in riverbank soil. By experimenting with the blocking effects and lateral diffusion of Cu^{2+} in soil

116 columns of various sizes, a PVC pipe (length 20 cm, inner diameter 1.6 cm, and outer diameter 2 cm) was used

117 to make a soil column for simulating the migration and distribution characteristics of copper. Sieve plate was

118 placed at the inlet end and outlet end of the column (upper sieve plate prevents the water from impacting the soil

119 sample, and the lower sieve plate prevents the soil sample from flowing down). Sand (0.3 cm) was filled between

120 the upper sieve plate and the soil sample, and between the lower sieve plate and the soil sample to prevent the

121 soil sample from blocking the micro-pores on the sieve plate. The flow rate of the Cu^{2+} solution was controlled

122 by the flow meter in the pipeline. The specific schematic diagram is shown in Fig. 2.

Experimental design

124   P and EP were added to the bank soil samples of GY, NB, JL, HC, MY, SN, GA, and DZ, respectively,

125 at a mass ratio of 1%. They were mixed evenly with original bank soils as contrast (CK), thus resulting in 24

126 kinds of amended soil samples, namely, GY_{CK} (GY soil), GY_P (GY soil + 1%P), GY_{EP} (GY soil + 1%EP), and

127 so on. The column experiment was conducted to simulate the migration and geochemical characteristics of

128 copper in each amended soil sample. Each treatment was repeated three times.

Experimental methods

130   The amended soil samples were uniformly loaded into the soil column to maintain the same weight and

131 density, with a weight of 48 g, a density of 1.19 g/cm^3, and water content of 1.5–2.2%. A fluid reservoir

132 containing 500 mg/L of $CuSO_4 \cdot 5H_2O$ was placed 1 m above the soil column and connected by a hose. The Cu^{2+}

133 solution switch was turned on to control the natural flow rate. The Cu^{2+} concentration at the outlet of the soil

134   column was measured every day at same time until the Cu^{2+} concentration was equal to 500 mg/L. Then, the

135   total leaching time and volume of the Cu^{2+} solution were determined. Next, the Cu^{2+} solution in the reservoir

136   was replaced with deionized water to wash (12 hours) the residual Cu^{2+} solution in the soil sample pores. After

137   the experiment, the soil column was divided into four parts: 0–5 cm, 5–10 cm, 10–15 cm, and 15–20 cm from

138   top to bottom. The soil samples of each part were air-dried and passed through a 60-mesh sieve. Then, the copper

139   content in exchangeable, carbonate, iron–manganese oxide, and the organic matter forms of the four parts were

140   determined (*Ari & Anne, 2005*; *Silveira et al., 2006*; *Perlatti et al., 2014*).

141   Cu^{2+} contents in plant samples were determined via Hitachi Z-5000 (Japan) flame atomic absorption

142   spectrophotometry, and background absorption was corrected through Zeeman effect. The above determination

143   was inserted into the standard solution for analysis and quality control.

RESULTS

Copper penetration characteristics

146   The results in Table 2 showed that as Cu^{2+} passed through the soil column, the balance time of copper

147   (when the Cu^{2+} concentrations at the inlet and outlet are identical) in each soil column was between 68 and 208

148   hours. For the same soil samples, the time required for copper penetration equilibrium in the soil column showed

149   the trend of EP-amended > P-amended > original soil (CK). In addition, the balance time of EP- and P-amended

150   soil is greater than that of CK. The average flow rate was opposite to the equilibrium time, which showed a trend

151   of CK > P-amended > EP-amended soil, and the average flow rate was between 9.7 and 18.9 mL/h. In general,

152   the addition of P and EP in the soil prolonged the penetration time and reduced the penetration velocity.

153   However, the comparative effect of the two materials showed that the adsorption performance of EP for copper

154   ions was stronger than that of P. Given that EDTA is an acidic organic compound, it can chelate with almost all

155   heavy metal ions to form a stable compound. Among the metal chelating agents, the chelating effect of copper

156   is significant (*Zhang et al., 2018*) .

157   For the same soil sample, the balance time showed a higher to lower trend, i.e., JL > SN > MY > GA > DZ

158   > NB > GY > HC, while the average velocity was opposite to the balance time (Fig. 3). The balance time of the

159   HC soil sample to reach equilibrium was the shortest, and the average flow rate was the largest. This outcome is

160   mainly because the pH value of the HC soil sample was acidic; the free copper in the soil was increased, and the

161   cation exchange capacity (CEC) of HC soil was small (*Arias et al., 2006*), which was not conducive to the

162   adsorption and immobilization of copper in the soil column. However, the CEC and clay content of JL soil

163   sample was higher (Table 1). Thus, the adsorption of copper was stronger, which was conducive to the adsorption

164   and immobilization of copper.

Vertical distribution of copper

166   After the penetration test, the soil columns were divided into four parts: 0–5, 5–10, 10–15, and 15–20 cm

167   from top to bottom. Copper in exchangeable, carbonate, and iron–manganese oxide form decreased from top to

168   bottom, as shown in Figure 4. Among all forms of copper, the carbonate form decreased most, followed by the

169   exchangeable and iron–manganese oxide forms. The organic matter form was the weakest (Fig. 4). The

170   distribution curve of copper on P-amended soil was relatively concentrated, while most of the copper distribution

171   curve was dispersed on EP-amended soil. Copper in exchangeable and carbonate forms on CK changed

172   remarkably compared with P- and EP-amended soil, which proved that P and EP played a certain role in altering

173   the distribution rule of copper forms in the soil column.

Copper accumulation characteristics

175   After leaching, the cumulative copper content in the mixed soil samples ranged from 21.70 to 45.88 g/kg

176   (Fig. 5). Furthermore, the copper content showed a trend of JL > SN > MY > GA > DZ > NB > GY > HC. The

177   results were consistent with the trend of balance time, which were contrary to the results of average velocity.

178   Thus, a longer balance time resulted in stronger copper adsorption and higher copper accumulation content in

179   the soil column. The copper content in different soil samples showed a trend of EP-amended > P-amended >

180   CK. The results demonstrated that the addition of P could enhance the ability of soil to accumulate copper. The

181   main reason is that this addition increases the content of organic matter in the soil, thus enhancing the

182   complexation of copper ions in the soil samples. Compared with P, EP-amended soil has stronger adsorption

183   capacity for copper. This characteristic may be due to the increase in porosity and specific surface area of soil

184   by the added material of P and EP, which provides a powerful condition for the adsorption of copper ions (*Zhang*

185   *& Zhan, 2012*; *Hu et al., 2016*); In addition, EP can form metal complexes with heavy metals, which ultimately

186   enhances the adsorption capacity of copper. The proportions of different copper forms in the soil samples varied.

187   Among them, the carbonate form accounted for the highest at 46.01%, followed by the exchangeable form

188   accounting for 25.96% and then the iron-manganese oxide form (16.52%). Finally, the organic matter form

189   (11.51%) was relatively small. This proportion was mainly related to a higher amount of carbonates in the soil

190   sample and the ability to exchange ions.

191   **DISCUSSIONS**

192   **Correlation between soil physicochemical properties and Cu froms**

193   Soil pH, CEC, total organic carbon (TOC), and specific surface area have important effects on the chemical

194   forms of copper, as shown in Fig 6. On the one hand, the results showed that the CEC of soil was significantly

195   correlated with the contents of exchangeable copper and carbonate copper in different soils. Moreover, the clay

196   content had a significant correlation with exchangeable copper. On the other hand, the correlation between pH

197   and specific surface area and various forms of copper content in soil was non-significant. The results showed

198   that CEC had a great influence on the copper content in soil samples, and pH and specific surface area had little

199   impact on the copper in the samples. The above results were mainly because of CEC, which could provide the

200   number of adsorption sites on the soil surface. The larger number of adsorption sites, the stronger the ions in the

201   exchangeable form were (*Lu et al., 2014*). TOC and copper contents in the soil sample were negatively

202   correlated. The TOC content in the soil sample occupied the adsorption point of the tested soil, thus inhibiting

203   the adsorption capacity of the tested soil to copper (*Teng et al., 2007*)

204   **Difference in copper adsorption**

205   Our results showed the variations of copper adsorption on different tested soils (Fig. 7). The absorption of

206   copper by natural soil depended on the physical and chemical properties of soil and clay content. The adsorption

207   capacity of clay for copper mainly drelied on the negative charge adsorption point between layers (*Cui et al.,*

208   *2010*). However, the adsorption capacity of the original soil for copper was low because of their low clay content.

209   P was mainly composed of cellulose, hemicellulose, and pectin. Research demonstrated that the metal adsorption

210   affinity of P mainly came from the surface bonding of cellulose and complexing action of pectin (*Mykola et al.,*

211   *1999*). Therefore, P-amended soil in this study had higher copper binding capacity than the original soil. After

212   modification by EDTA, the effective functional groups on P were increased, and the morphology was more

213   porous (*Qi, 2012*). Meanwhile, EDTA was able to form stable complexes with most heavy metal ions (Zhang et

214 al., 2018; *Li, 2014*), and improve the adsorption capacity of EP-amended soil samples for copper.

215 **CONCLUSION**

216   This study showed several key points, which described the effectiveness of amendments on the

217 immobilization of heavy metals. The balance time of copper in each soil column showed EP-amended > P-

218 amended > original soil. In addition, it presented JL > SN > MY > GA > DZ > NB > GY > HC at different

219 locations. The average velocity of copper on each soil column indicated a reverse trend with the balance time.

220 In the vertical distribution, copper contents in exchangeable, carbonate, and iron–manganese oxide forms

221 decreased with the increase of soil column depth, among which the carbonate form decreased most evidently.

222 Copper accumulation at various locations and on different soils presented the same trend with balance time. The

223 largest proportion was the carbonate form, followed by the exchangeable and iron–manganese oxide forms. The

224 organic matter form was the lowest. A significant correlation was observed between the CEC and the

225 exchangeable and carbonate forms of copper. Meanwhile, TOC and copper contents were negatively correlated.

226 **ACKNOWLEDGEMENTS**

231 **CONFLICT OF INTRESTS**

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

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Table 1(on next page)

Basic physical -chemical properties of the riverbank soils

Note: The average values are given. Soil humidity in the table is divided into four grades: dry, slightly moist, moist, and wet. The number of soil pores and roots was divided into three grades: large amount, defined amount , and small amount. Soil structure is divided into block, granular, flake, nucleus, and so on. CEC is the c ation exchange capacity, TOC represents t otal organic carbon, and SSA means s pecific surface area.

1

Soil samples	Longitude and latitude	Altitude (m)	Crop rotation	Soil humidity	Soil porosity	Soil structure	Root number	pH	CEC (mmol/kg)	TOC (g/kg)	SSA (m²/g)	Cu content (mg/kg)	Clay content (%)
GY	E105°55′18.94″ N31°45′6.12″	430.3	Peanu, corn	slightly moist	much	granular	little	8.16	120.72	15.75	90.34	18.84	10.74
NB	E106°09′1.38″ N31°17′48.79″	427.4	Chili, rice	slightly moist	little	blocky	little	7.99	118.22	28.16	110.44	13.80	9.22
JL	E106°06′37″ N30°42′19″	270.0	Corn, sweet potato	moist	much	granular	medium	7.70	204.08	12.28	130.21	16.32	12.51
HC	E106°17′30″ N29°58′23″	245.1	Sweet potato, green beans	slightly moist	little	blocky	little	6.56	100.69	25.83	89.34	24.74	7.28
MY	E105°03′25.6″ N31°08′57.43″	380.7	Corn, konjac	moist	little	blocky	little	7.80	122.53	25.01	98.25	19.68	9.27
SN	E105°38′17″ N30°27′45″	283.1	Corn, pterocarpus	moist	little	blocky	much	7.44	182.79	8.84	103.14	8.75	10.66
DZ	E106°57′20.07″ N30°51′38.5″	314.0	Corn, rice	slightly moist	little	granular	little	7.42	118.31	24.23	141.27	23.04	9.41
GA	E106°40′25″ N30°27′42″	0.0	sweet potato, corn	slightly moist	medium	granular	much	7.59	153.98	21.56	102.45	58.38	10.15

2

Table 2(on next page)

Leaching balance time and a verage velocity

1
2

Soil samples		Balance time (h)	Average velocity (mL/h)	Soil samples		Balance time (h)	Average velocity (mL/h)
GY	GY_{CK}	80	18.0	MY	MY_{CK}	128	14.1
	GY_P	122	15.3		MY_P	156	12.8
	GY_{EP}	132	13.0		MY_{EP}	180	11.0
NB	NB_{CK}	92	17.4	SN	SN_{CK}	140	13.4
	NB_P	120	14.1		SN_P	172	12.0
	NB_{EP}	144	12.5		SN_{EP}	192	10.3
JL	JL_{CK}	164	12.2	DZ	DZ_{CK}	108	16.4
	JL_P	184	11.4		DZ_P	136	13.7
	JL_{EP}	208	9.7		DZ_{EP}	152	11.7
HC	HC_{CK}	68	18.9	GA	GA_{CK}	116	15.6
	HC_P	96	16.3		GA_P	148	13.2
	HC_{EP}	122	14.3		GA_{EP}	164	11.1

Figure 1

Fig.1 Distribution map of sampling points
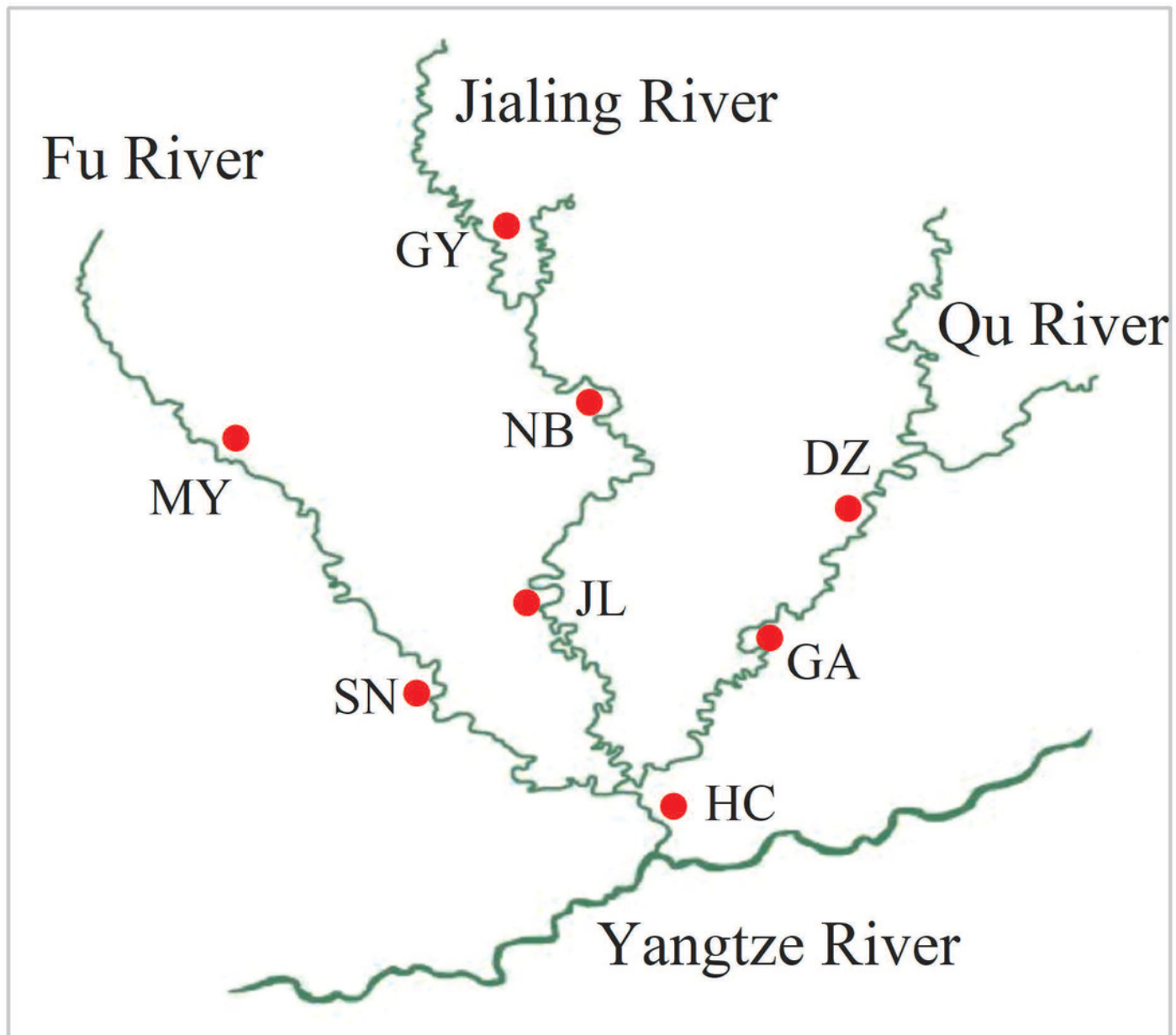
Figure 2

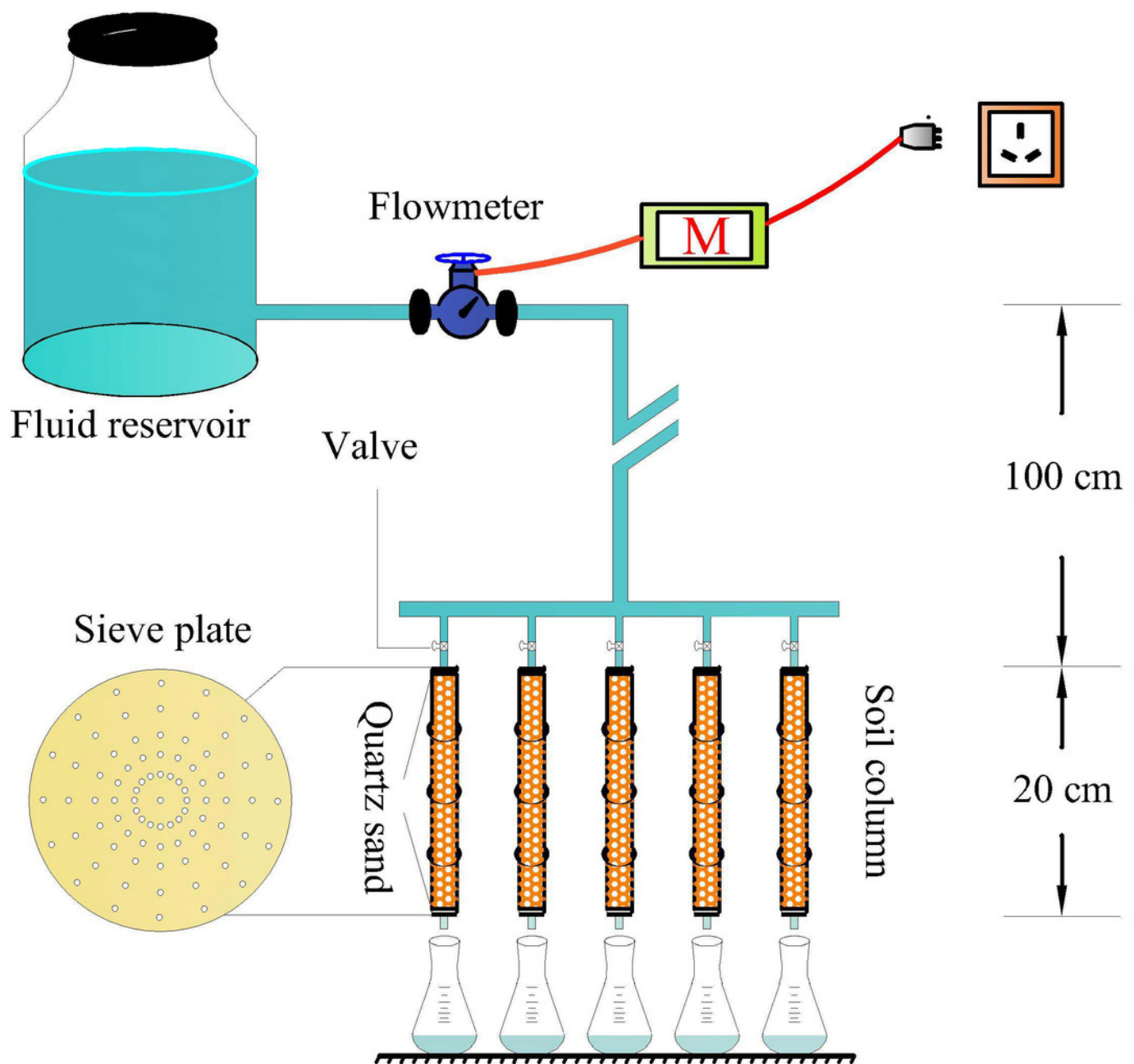Fig. 2 Schematic of the soil column structure

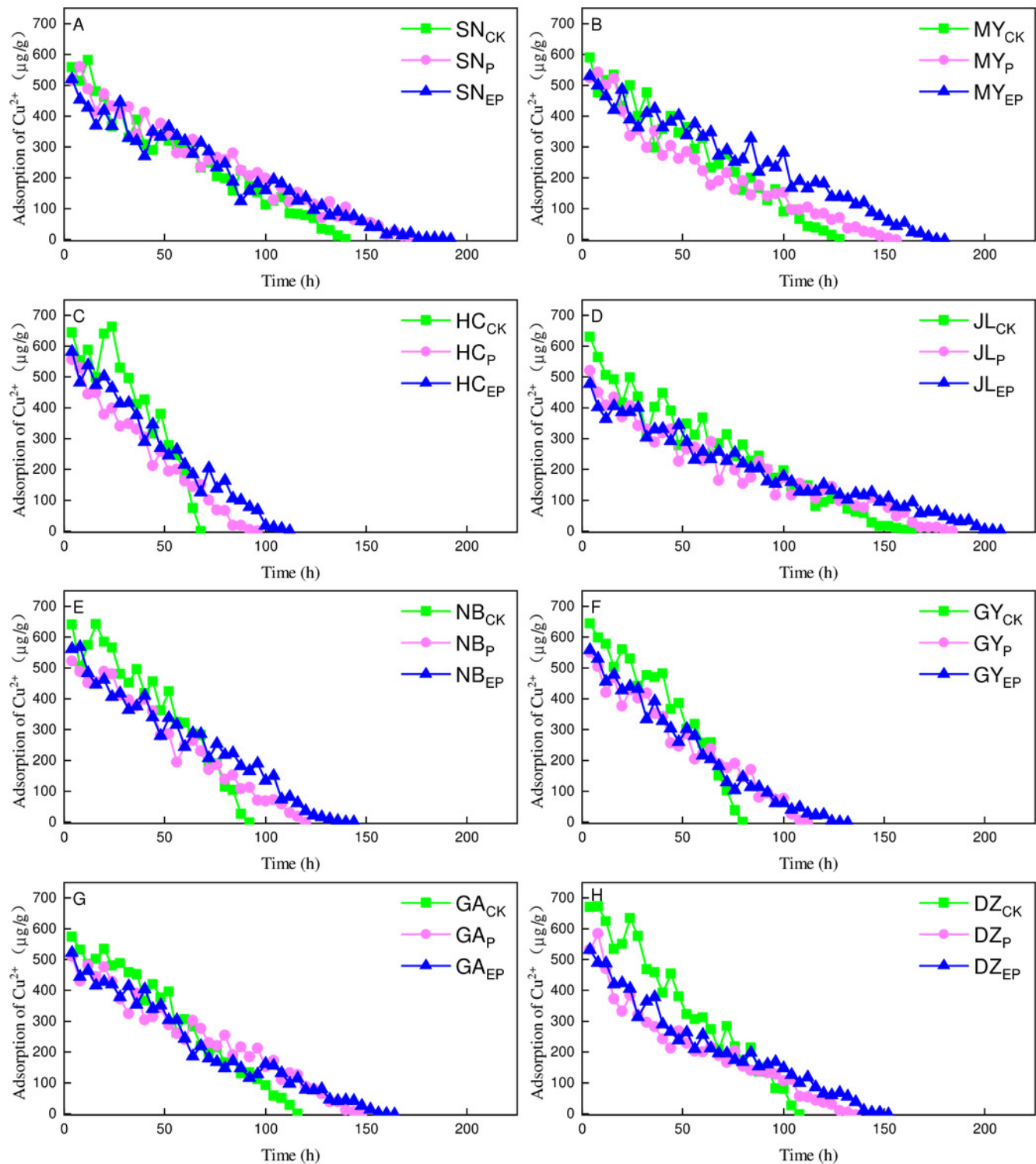# Figure 3

Fig. 3 Equilibrium time rule of each soil column

Figure 4

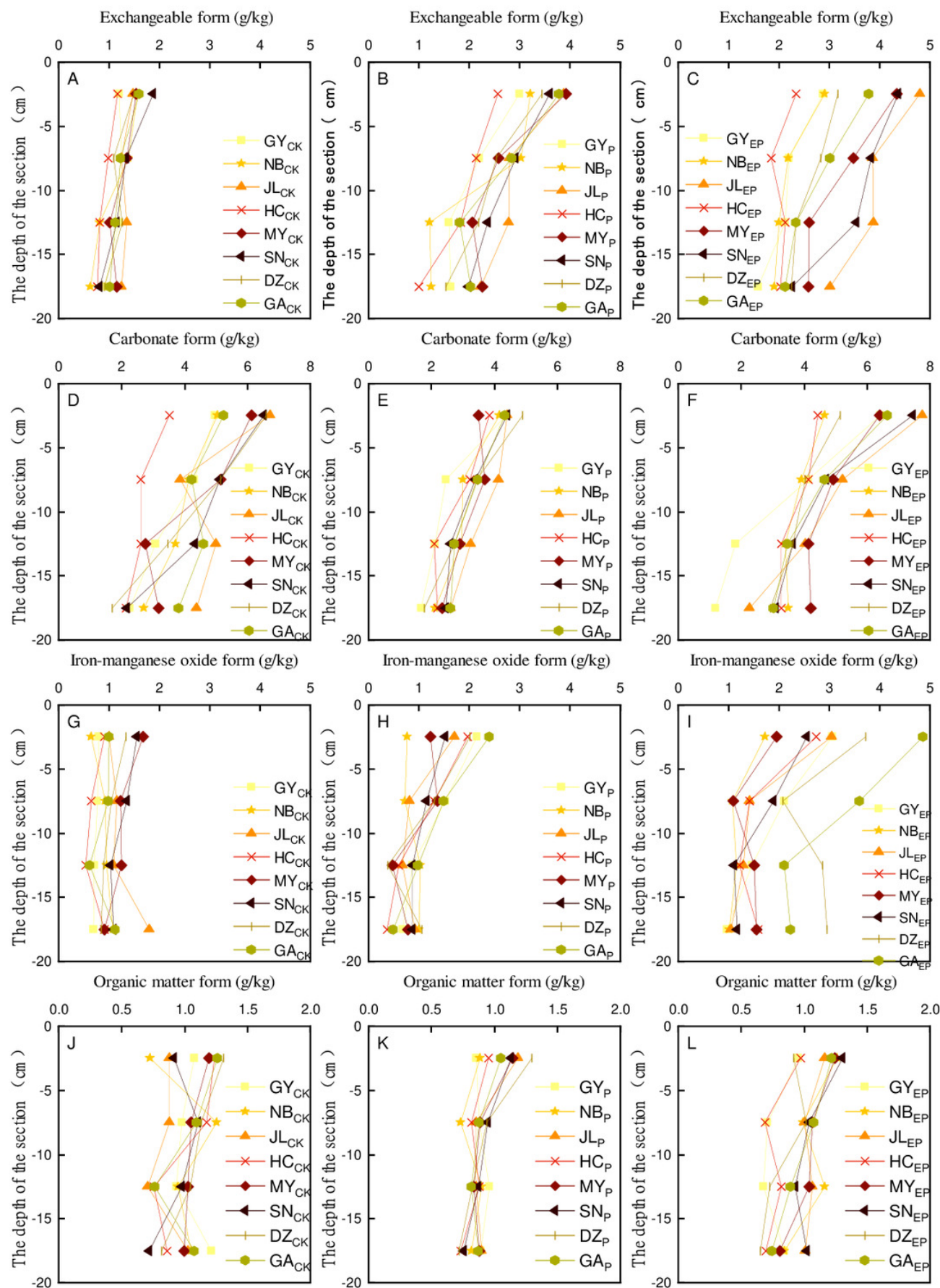Fig. 4 Distribution characteristics of Cu morphology in vertical section

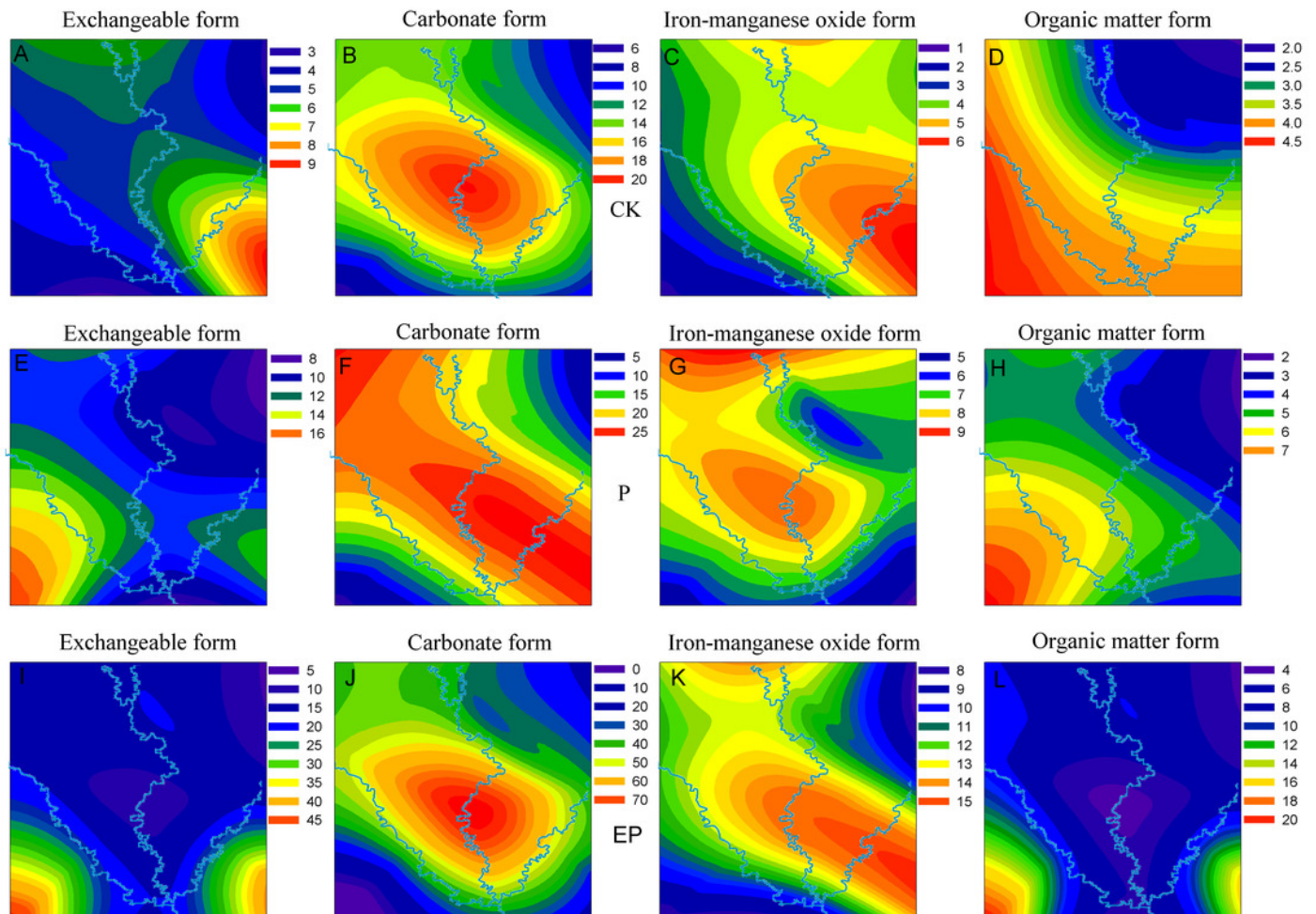# Figure 5

Fig. 5 Contents of various forms of copper

Figure 6

Fig. 6 Correlation analysis of soil physicochemical properties and Cu morphology. EX, CA, IMO, and OM are the acronyms for exchangeable, carbonate, iron-manganese oxide, and organic matter forms, respectively

Note: * and ** indicate a significant correlation at the level of $p = 0.05$ or 0.01. When $f = 7$ and $p = 0.05$ or 0.01, $r = 0.666$ or 0.798. The values are the same below .
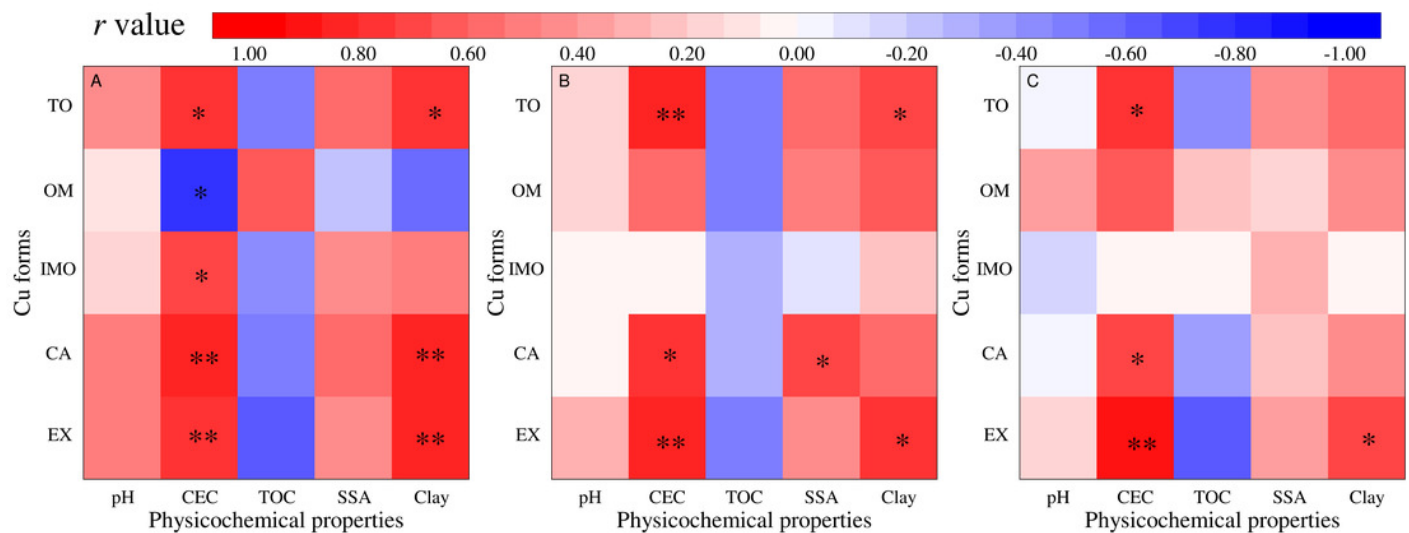
Figure 7

Fig. 7 Adsorption differences of copper on different soil samples