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Influence of thermal treatment on the bioavailability of Cu, Cd and Zn in polluted forest soils

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Abstract

The role of fire on the soil is a complex and comprehensive process. Fire has influences on soil physiochemical properties and hence the soil ecosystem. Meanwhile, forest soil faces an increasingly severe pollution problem due to the use of pesticide and fertilizer. The heavy metals transfer into soil and underground water and bio-accumulate in flora and fauna, which is of great concern due to the immediate risks to human and ecosystems health. This work aims to investigate the factor of heating temperature on the heavy metals in forest soils by using thermal treatment microscopically, in order to establish the correlation between the macro-scale and micro-scale research on the investigation of fire effect on heavy metals in soils; disclose the mechanisms of individual fire factor on heavy metals transformation by micro-scale experiments. Soil samples were taken from the upper layer (0-5cm) of the forest soil that situated in Huangshi Mining National Park, China where used to be a mining site and now reserved as a national park with vegetation recovery. However, the soils are still in the pollution state with high concentration of heavy metals, such as Cu, Cd, Zn, As, *etc*. The thermal interaction of heat is achieved by controlling the temperature and reservation time. In addition, the heating atmosphere with and without oxygen is also compared by using vacuum furnace and muffle furnace, respectively. Concentrations of heavy metals, compositions of soils are determined by ICP-MS and ICP-AES. Soils are dried and sieved. Other characterizing techniques include thermogravimetric analysis, dynamic laser light scattering, elemental analysis. The original concentrations of Cu, Cd, Zn were determined as 1303.41 mg/kg, 6.91 mg/kg, 927.1 mg/kg and 118.3mg/kg, respectively. Effect of heating on heavy metals displayed difference roles. Furthermore, the absence of oxygen may also change the fractions of heavy metals and reduce their bioavailability. The results of the effect of heating on heavy metals in soils by thermal treatment may shed light on the understanding of the mechanisms of wildfire effect on heavy metals in forest polluted soils which may provide the bias for the prediction of heavy metals transformation in the post-fire ecosystem and the exposure assessment of health risk. These mechanisms may shed light on the theory of forest fire ecology and provide measures for forest fire management and soil restoration.

Keywords: heat; heavy metals; bioavailability; soil pollution; fire ecology;

1. Introduction

Wildfire is a unique disturbance factor that plays a significant role on the evolution of earth ecosystem (DeBano et al, 1998). It can reduce the forest area and affect the biodiversity of flora and fauna in the burnt area. Soil experiences transformation in its physical, chemical and microbial properties, especially the modification of heavy metals and organic components. The organic matter can be decreased when temperature of soil reached to 300ºC.

Work of macro-scale fire on soil has been drawn great attention in various publications. Debano *et al*., (2000) and Malkinson *et al.* (2011) discussed the mechanisms of fire and soil heating on water

repellency in wildland environments. Hydrophobic compounds were generated and migrated into soil deeper during the fire event, which may increase the water repellency. Meanwhile, the higher water content can provide a positive role on the protection for the soil against fire (Badia et al, 2017). Soil temperature and heat duration as a function of soil moisture and soil texture were identified to indicate that 20% volumetric moisture or greater was an effective means for limiting lethal heating in soils (Busse et al 2010). In spite of the damage by the fire, wildfire is considered that it can improve the soil quality (Stankov et al, 2011). Fire can increase soil pH and the bioavailability of N, P, K, Ca, nutrtion elements. However, few of the work were focused on the effect of fire on Fe, Mn, Cu, Zn, Co, B, *et al.*, especially the heavy metals in polluted soils. Transformation of forms of Mn in burnt soils were observed (Parra and Lopes, 1996). The transformation of Fe, Mn, Cu, Zn, were showed of irregularity. Macroscopic wildfire research under filed conditions is defective with various factors (vegetation, litter depth, soil water content, soil pore network, *et al.*) that may affect the soil properties comprehensively during fire conditions (Busse et al 2010; Archibold et al, 1998; Campbell and Jungbauer, 1995). Furthermore, literature has reported that the thermal remediation can alter the soil properties (O'Brian et al, 2018), indicating that the thermal treatment may change the forms of heavy metals in the soils.

Thus, this work aims to investigate the effect of temperature on the fractions of heavy metals in forest soils by using thermal treatment microscopically, in order to establish the correlation between the macro-scale and micro-scale research on the investigation of fire effect on heavy metals in soils; disclose the mechanisms of individual fire factor on heavy metals transformation by micro-scale experiments.

2. Materials and Methods

2.1. Soil description and soil sampling

Soil samples were taken from the upper layer (0-5cm) of the forest soil that situated in Huangshi Mining National Park, China were historically under long-term mining operation. Concentrations of heavy metals, such as Cu, Cd and Ni, in the Huangshi Mine National Park were determined exceeding the criteria concentration in 2007 (Han, 2007).The main vegetation in this area are schima superba, locust tree and camphor tree. The soil type can be classified to red earth. Samples with 11 sampling points were taken in "S" shape and contained in the polyethylene box. Subsequently, soil samples were air-dried, grounded, sieved by 150µm particle size, and stored in a drying vessel before sample characterization and thermal treatment.
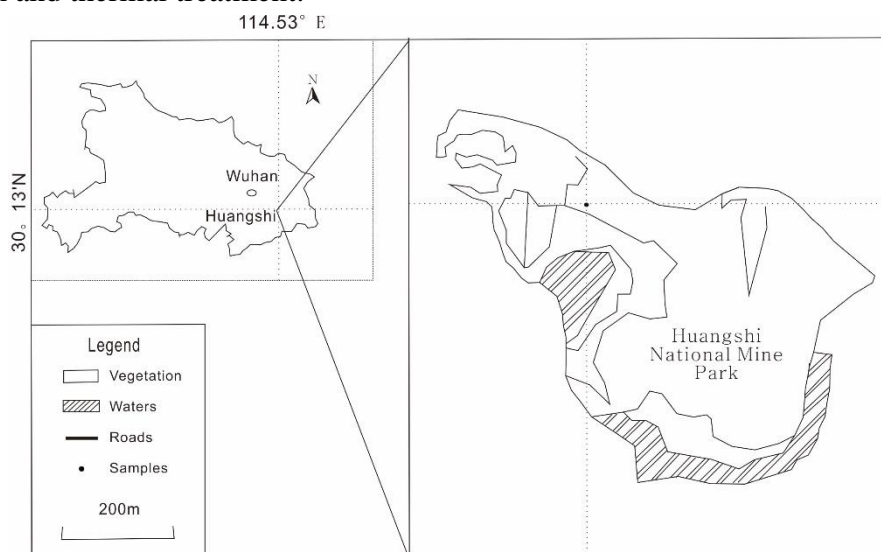

Figure 1 - Location of study area

Chemical reagents include acetic acid, hydroxylamine hydrochloride, ammonium acetate, $HClO_4$, HCl, HNO_3 etc. All the reagents are analytic. Mili-Q water (18 MΩ·cm) was used for all solution preparation.

2.2. Thermal treatment of soil samples

8g soil sample in the crucible was put in the tube furnace (MXG1200-S40), under N_2 atmosphere. The parameters included heating temperature and reservation time, which were set at 200, 300, 400, 500 °C and 30, 60, 90 min, respectively. As a contrast, the group of muffle furnace was set at 500 °C. The soil samples after heating were cooled to room temperature and reserved in drying vessel for further characterization.

2.3. BCR extraction method

In this study, modified four-step BCR method were applied to extract the heavy metals in the soil samples. Accordingly, 0.5 g of dry soil was extracted in a 50-mL centrifuge tube with the corresponding extracting solution. The first fraction (exchangeable fraction) was considered as most soluble and 0.11 mol/L acetic acid was used as the extractant. The second extraction (Reducible fraction), from which the reducible elements were obtained, was performed using 0.5 mol/L hydroxylamine hydrochloride. In the third extraction (Oxidizable fraction), the oxidizable fraction was obtained and 8.8mol/L ammonium acetate (pH=2) was used following oxidation with 8.8 mol/L H_2O_2. Finally, the fourth extraction (residual fraction) was perform by using Milli-Q water. All the samples were agitated at room temperature by using end-over-end shaking. Subsequently, all the supernate of soil samples were determined by inductively coupled plasma emission spectrometer(ICP).

2.4. Charactersation methods

TGA (Thermogravimetric Analysis, Perkinelmer sta6000) was used to analysis the weight loss of soil samples. ICP (Inductively Coupled Plasma Emission Spectrometer, Agilent 5100) was applied to determine the concentration of the heavy metals in the soil sample before and after heat treatment. Other equipment used included centrifugal machine, table concentrator, *etc.*.

3. Results and discussion

3.1. Fractions of heavy metals in soil samples before thermal treatment

Total concentrations of Cu, Cd, Zn in the soil were determined to be 1303.41 mg/kg, 6.91 mg/kg, 927.1 mg/kg and 118.3mg/kg, respectively, which far exceeded the soil criteria of China. The heavy metal fractions of original samples are shown in Table 1. The percentage of the fraction distribution of heavy metals displays in Figure 1. The main form of Cd is residual, so Cd is very stable in the soil sample. The order of concentrations of different fractions of Cu is as following: the reducible > oxidation > the residual > the acid soluble. Cu in the sample has a relatively high bioavailability, The order of concentration of different fractions of Zn shows: the residual > the reducible > oxidation > the acid soluble. The available fractions of heavy metal are similar to Cu, both of which can cause a risk to ecosystem and human health.
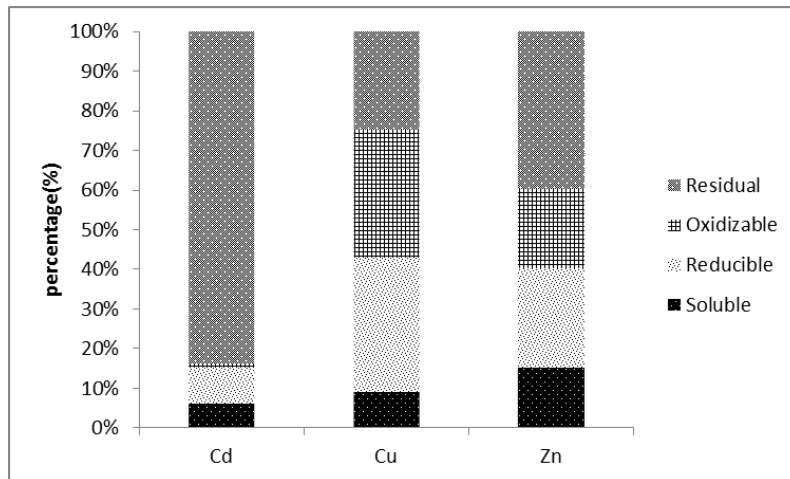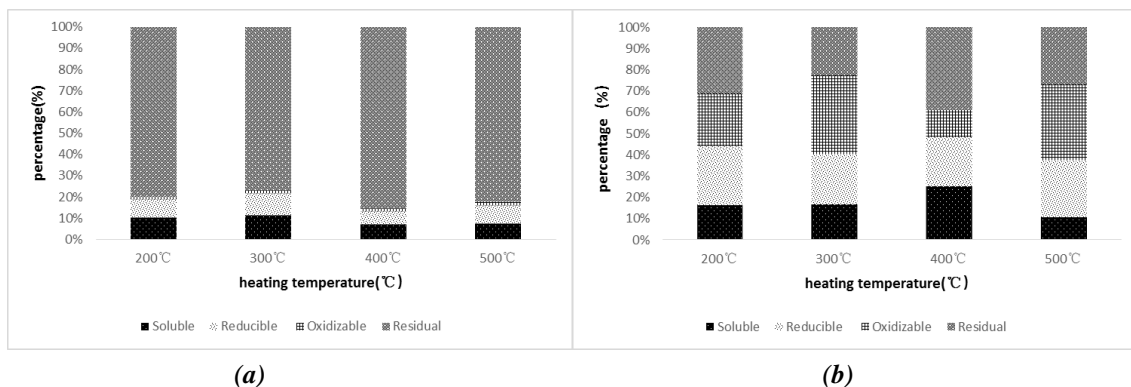
Figure 2 - The fraction distribution of Cd, Cu and Zn

Table 1 concentrations of copper, cadmium, zinc in the soil samples

Heavy metals	Soluble (mg/kg)	Reducible (mg/kg)	Oxidizable (mg/kg)	Residual (mg/kg)	Total (mg/kg)	Total in Criteria (mg/kg)
Zn	17.43	28.98	23.08	46.02	927.1	500
Cu	116.45	442.75	421.25	322.95	1303.41	400
Cd	0.42	0.63	0.07	5.79	6.91	0.3

3.2. Effects of temperature on heavy metal fractions

Distribution of Cu,Cd and Zn in the aqueous extracts and solid residue from sequential extraction of soil samples are shown in Figure 2. Concentrations of available fraction are shown in Figure 3. It can be easily found that the trend of avaiable fraction concentration of three heavy metals is decreased with the increase of temperature, which is same with Yang's results [13]. The increase of Cu and Cd from 200℃ to 300℃ may due to the weight loss during temperature increasing, which can be obviously seen in Figure 4. The changes of fraction distribution is rather complex, but compared to at 200℃, the percent of available fraction in Cd,Cu and Zn is lower when the constant heating temperature was set at 500℃,which can indicate that the relative high temperature is able to reduce the bioavailability of heavy metals.
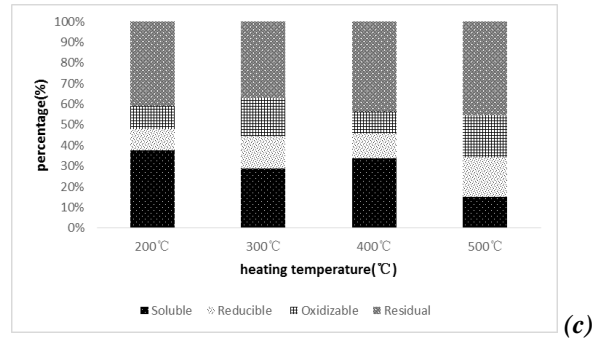

(a)

(b)

(c)

Figure 2 - Effects of temperature on the distribution of Cd(a),Cu(b), and Zn(c).
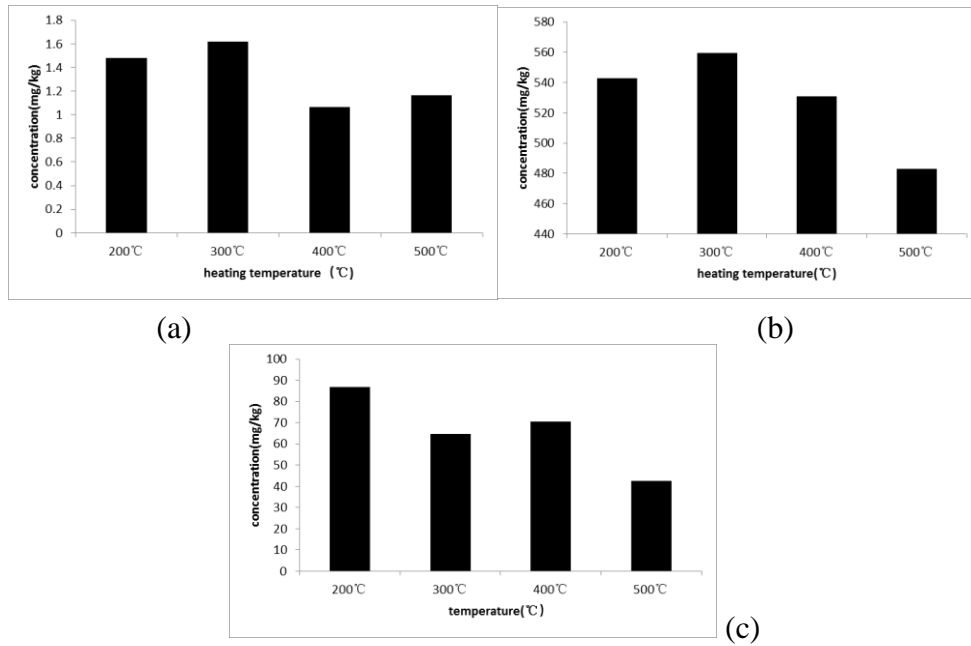

(a)

(b)

(c)

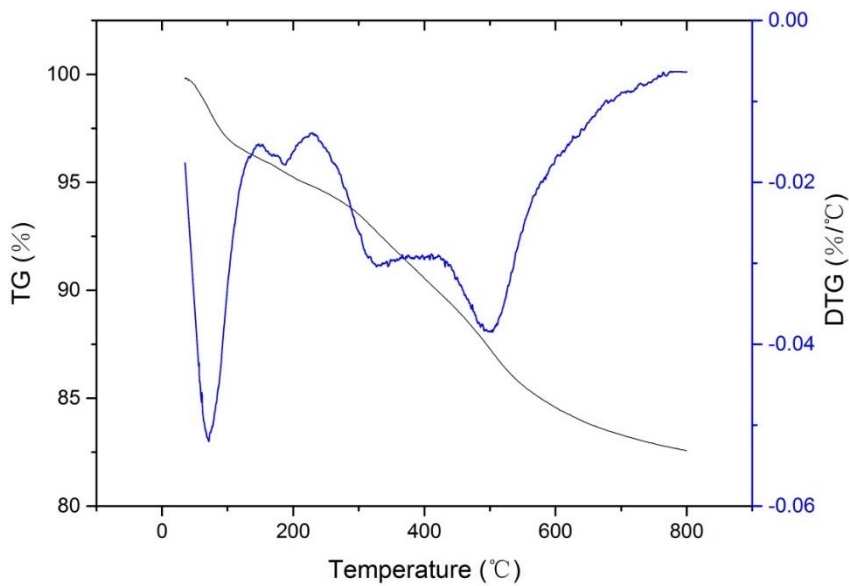**Figure 3 - Effects of temperature on available fraction concentration of Cd(a),Cu(b), and Zn(c).**

Figure 4 - The result of TGA(Thermogravimetric Analysis)

3.3. Effects of heating time on heavy metal fractions

Figure 5, 6 show the effects of reservation heating time on heavy metal fraction distribution. The trend of available fraction of Cu and Zn was decreased when the heating time increased. In addition, the distribution of Cd was almost constant because the residual fraction of Cd was very high in original soil sample. The available concentrations of heavy metals were decreased with the heating time shown in Fig…, which indicated that long-time heating might benefit for decreasing heavy metal bioavailability. Besides, compared to Cd and Zn, the change of Cu was not obvious, which may be the result of that Cu possesses a relatively high boiling point.
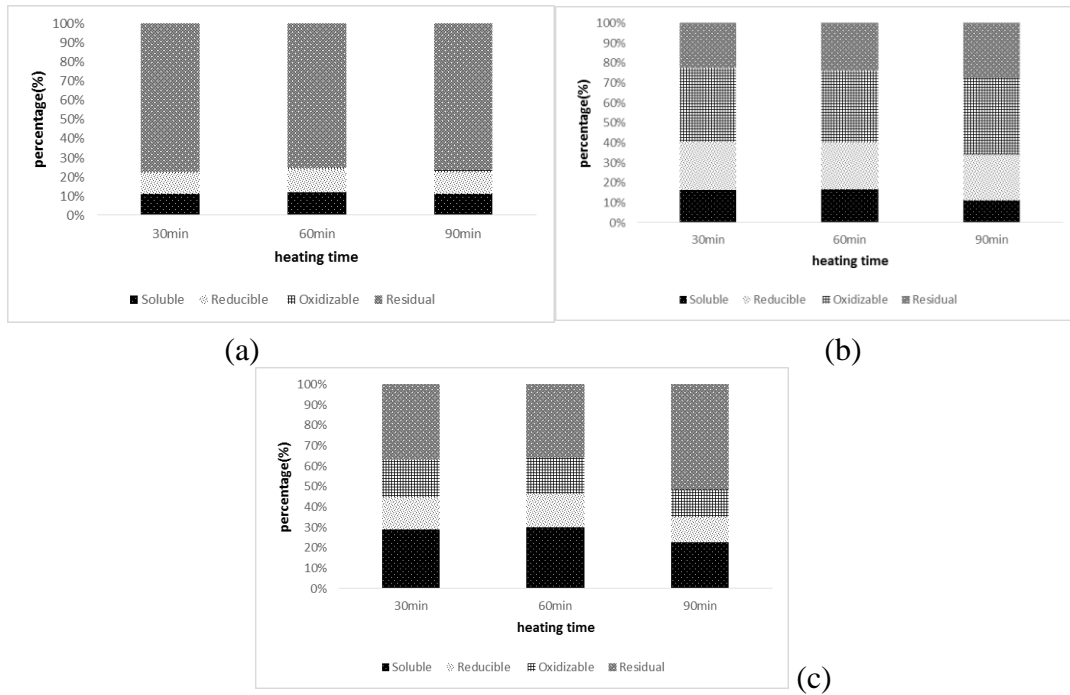

(a) (b) (c)

Figure 5 - Effects of temperature on the distribution of Cd(a), Cu(b), and Zn(c).
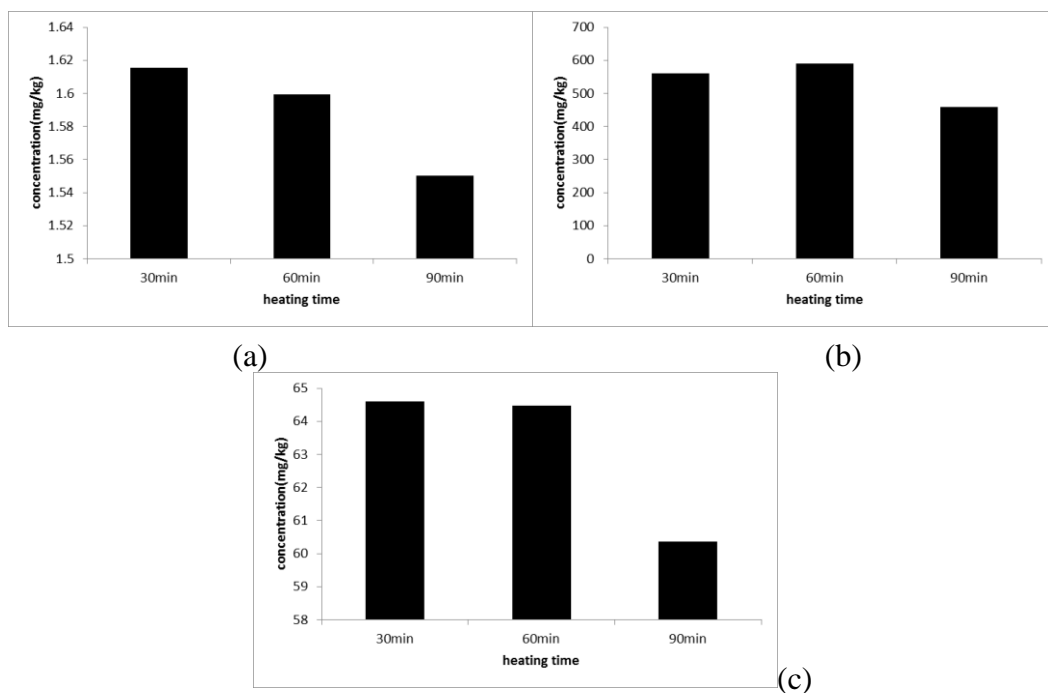

(a) (b) (c)

Figure 6 - The influence of heating time on available Cd(a), Cu(b), Zn(c) concentration

3.4. Oxygen effect

Oxygen effect on the heavy metals in soils were performed and compared by muffle furnace and tube furnace, shown in Figure 7. The available Cd concentrations of the tube furnace and muffle furnace showed little difference with values of 1.16 and 1.27 mg/kg respectively. However, there was an obvious difference for Cu and Zn. The available Cd concentrations of tube furnace and muffle furnace are 483.1046, 596.5688mg/kg respectively. For Zn, the concentration was 42.56 and 72.20mg/kg, respectively. Such results indicated that absence of oxygen may play a role on reducing the heavy metal bioavailibity.
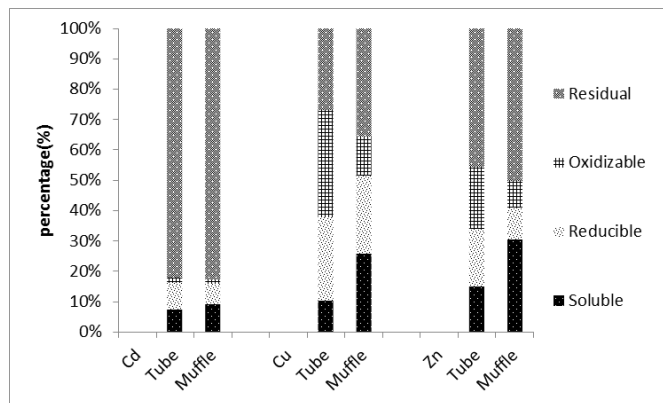

Figure 7 - The comparision between tube furnace and muffle furnace

4. Conclusions

The work investigated the effect of heating time and reservation time on heavy metals in forest polluted soils by using thermal treatment method. The original concentrations of Cu, Cd, Zn were determined as 1303.41 mg/kg, 6.91 mg/kg, 927.1 mg/kg and 118.3mg/kg, respectively. Effect of heating on heavy metals displayed difference roles. After thermal treatment, concentration of Cd was increased after 200, 300, 400, 500 ℃. which may due to the weight loss during heating. Percentage of fractions the bioavailability of Cu, Cd, Zn was no noticeable. Furthermore, the absence of oxygen may also change the fractions of heavy metals and reduce their bioavailability. The results of the effect of heating on heavy metals in soils by thermal treatment may shed light on the understanding of the mechanisms of wildfire effect on heavy metals in forest polluted soils which may provide the bias for the prediction of heavy metals transformation in the post-fire ecosystem and the exposure assessment of health risk.

5. Acknowledgement

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