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The Effect of Ozone-Electric Treatment on the Enrichment and Transfer of Heavy Metal Cu in Sludge

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Abstract

In order to explore a safe, effective way to use sludge as agricultural fertilizer it is necessary to effectively separate and remove the heavy metals embedded in sludge. In the study, the ozone-electric two-stage treatment was used to transform heavy metal copper in the sludge, and then the treated sludge was used for maize production and the transferring of Cu in cultivation medium and plants, and the enrichment effect of Cu in plant were investigated. According to composition of culture substance, five treatments were set in maize planting experiments: CK, Agricultural soil without addition; T1, Agricultural soil supplemented with raw sludge; T2, Agricultural soil treated with ozone sludge; T3, Agricultural soil with ozone treated and electric treated sludge; T4, Agricultural soil added with common organic fertilizer. The results showed that in different treatments, the Cu content of organs showed the order of root> stem> leaf> cob> grain. Comparing root Cu content, the lowest was in T1 treatment, which was 11.60 mg/kg, while the lowest of grain Cu content was found in CK treatment, which was 1.36 mg/kg. In the upper, middle and lower soil layers, the highest and lowest Cu content was in T4 and CK, respectively. In both middle and lower soil layers, the Cu content of T1, T2 and T3 sludge treatments had a trend of T1>T2>T3; the difference of the Cu enrichment ability between different organs is not significant in the same soil layer. From each treatment, the Cu enrichment ability of plant of CK was higher than that of other treatments. According to the ability of Cu transferring to the above-ground part of plant, treatments are ranked as CK>T3>T4>T1>T2. The transferring of Cu from soil to plant was mainly affected by fertilizer level and the transferring rate of Cu from soil to stem, leaf and root was relatively high, but it was hardly affected by sludge. In summary, after ozone-electro treatment, the application of sludge does not significantly affect the Cu content in maize, and the Cu content in each treatment does not exceed the limit value of agricultural production.

Keywords: electro treatment, village sludge, heavy metal, copper, sludge application in agriculture

1. Introduction

More and more domestic sludge is produced with the advancement of China's urbanization, and technologies on how to dispose the sludge safely and economically have been widely concerned across our country. Sludge, coming from sewage, is a kind of anisotropic material, composing of organic residues, bacteria, inorganic particles, colloids, etc. In particular, sludge contains various organic and inorganic plant nutrients (Su, et al. 2012), which is capable of improving soil fertilities (Yang, et al. 2009; Sharma, et al. 2017), so the use of sludge as fertilizer is the most potential disposing way. Considering economic benefits, environmental safety and sludge properties, now there are 54% of the sludge used as fertilizer in the UK, and there are 60% in USA. In China, the use of sludge as fertilizer accounts for 44.83% of total sludge volume (Zhang, et al. 2015). Sludge, however, may contain a large number of pathogenic microorganisms (Strauch, et al. 1993), polycyclic aromatic hydrocarbons (PAH) (Czekala, et al.1999), trace metal elements (Bien, et al. 2014), etc. For the pollutants from sludge, heavy metals have a particularly significant impact on the quality of crops, for they are highly toxic (Zhang, et al. 2015), hardly decomposed by microorganisms, and enriched in crops if applied in farmland, doing harm to human (Liang, et al. 2009), and copper (Cu) is a typical heavy metal elements from sludge. Cu is common in biological tissues, existing as organic complexes, in particular as metalloproteins, and functions as enzymes during life processes. But too many Cu elements are hazardous to human healthy, because copper ions will denaturate proteins and copper sulfate ($CuSO_4$) has a stimulating effect on the gastrointestinal tract, causing damage to human health. The potential ecological risk limits the utilization of sludge as agricultural fertilizer.

Previously, many technologies have been explored to remove heavy metals from sludge, including biological leaching (Zhang, et al. 2016), chemical leaching (Xu, et al. 2014), phytoremediation (Gao, et al. 2013), stabilization(Su et al. 2010), electric remediation (Yu, et al. 2009; Xiao, et al. 2014; Yang, et al.2008; Peng, et al. 2010), and so on. Electric remediation technology is an emerging method to treat heavy metal in sludge in recent year and gets good result (Yang, et al. 2008). When using this technology, inert electrodes are placed into the solid-liquid system of sludge, the metal cation will enrich in the cathode area in direct-current electric field, and the concentrated heavy metals can be removed from sludge. Most heavy metals in sludge are in stable states such as Fe-Mn compound, organic matter and residues (Guo, et al. 2014). The existing states of heavy metals are closely related to the migration rate in electric field, and heavy metal particles in exchangeable forms migrate fast. Ozone aeration is another useful technology to dispose heavy metals of sludge. It can not only kill pathogenic bacteria, but also destroy the floc structure of sludge to change heavy metals from fixed state into soluble state (Zhao, et al. 2009). In this paper, we combined electric remediation technology with ozone aeration to remove Cu from sludge; the disposed sludge was further used as fertilizer to culture maize to explore the transformation rule in plants and enrichment law in soil. This study will provide reference for the actual use of sludge in agriculture.

Table 1. Comparison of Removal Methods of Heavy Metals in Sewage Sludge

Methods	Advantages	Disadvantage	Applicability	Influencing factor	Main technical parameters
Bioleaching	Less acid consumption, simple equipment, low operating cost, good removal effect, non-toxic byproducts	Long retention time and high concentration of heavy metal leachate	The application range is wide and can remove pathogenic bacteria at the same time	Temperature，pH	Temperature，pH，The initial concentration of the matrix
Chemical extraction	Easy to master, simple operation, short time consuming	High operation cost, difficult operation, large amount of chemical reagents, easy to cause secondary pollution	Can reduce the fertilizer value of sludge	Properties and chemical speciation of heavy metals	Properties and concentration of the extractant
Plant extraction	Environmentally friendly, low cost	Plant growth was too slow to meet treatment requirements	It can only be used as an auxiliary method and is not suitable for sludge with high residual heavy metal content	Morphology of heavy metals	Species of plants
Heavy metal passivation	Improve the stability of metal, reduce the toxicity of heavy metals	The cost of investment is high, there is a shelf life and the risk is still there in the long term.	It is suitable for short-term solution of metal poisoning to soil and crops and belongs to emergency measures.	Soil pH, metal form, metal type	The stability of metal form, the selection of excipients and dosage.
Ozone - Electric power technology	Less reagent, high removal efficiency, short treatment time	High concentration of heavy metal attachment, electrode polarization, high operating cost	Suitable for all kinds of digestive sludge without flocculation treatment.	Speciation of heavy metals and pH value of solution	Current, voltage

2. Methodology

2.1 Experimental Materials

2.1.1 Sludge Sample

Sludge sample was collected from Tianjin Sewage Disposal Plant. The sample was processed in advance before treatment. Firstly, they were adjusted the pH to 2 with dilute sulfuric acid (2 mol/L), rinsed with distilled deionized water, and air-dried. Secondly, a small amount of sample were ground into fine powder, sifted by a 2-mm sieve to remove refractory particles, and fully mixed and stored in a plastic container at room temperature of about 23℃. The main compositions of original sludge are showed in Table 2.

2.1.2 Organic Fertilizer

Organic fertilizer is from a Tianjin organic fertilizer company, and the fertilizer is produced for crop production. The main components are presented in Table 2.

2.1.3 Maize Cultivation Soil

Soil for maize planting was taken from an experimental farm (E116°58′17.31″, N39°08′12.02″), located in Yangliuqing Town, Xiqing District, Tianjin. The soil is dried and processed by passing through a 1-mm sieve before seed planting. The soil type is loam, pH is 7.98, soil layer thickness 0-40cm, particle size grading (9% clay, 44.6% silt, 46.4% sand), and contains organic matter of 18.25 g/kg, total nitrogen of 1.16 g/kg, available phosphorus of 41.60 g/kg, available potassium of 168.3 mg/kg, and copper of 44.83 mg/kg.

2.2 Experimental Design

2.2.1 Ozone Aeration (Ozonation)

The core of the ozone treatment includes a high-purity oxygen generator, a high-pressure ozonizer and an air and liquid mixer. The rated ozone output of this experimental system is 750L/min, the ozone concentration can reach 50 mg/L, and the power consumption is 0.3kW/h.

To recover the original property of sludge, prepared sludge sample (semisolid) was diluted from 40% of solid substance to 1% before ozone aeration. The diluted sludge sample had pH of 7.32, and contained Electrical conductivity value (EC) of 1.81 ms/cm, Chemical oxygen demand measured by potassium dichromate method (COD_{Cr})of 4049.13 mg/L, NH_4^+-N of 19.50 mg/L, NO_2-N of 0.02 mg/L, NO_3-N of 4.37 mg/L, total nitrogen of 330.88 mg/L, and total phosphorus of 146.34 mg/L. Ozone of 50 mg/L was used for sludge ozonation treatment; samples were tested at 0, 10, 20, 30 and 40 min after ozone aeration and were considered as five treatments.

2.2.2 Electric Treatment

After ozone aeration, sludge sample was further subjected to electric treatment with 48 V direct-current. A self-designed monomer experimental tank is used for electrodynamic separation，which has anode and cathode graphite plates that can be inserted or removed freely. The positively charged metal cations and micelles will eventually form massive deposits in the cathode region, which will be attached to the cathode plate, while the insoluble precipitated and attached to the graphite plate are separated heavy metal deposits. According to time length, five treatments (10, 30, 60, 120, and 240 min) with three replications were conducted, with original sludge sample was used as control. After treated, sludge sample was dried again, ground, and sifted by 100-m sieve for Cu measurement.

Table 2. Components of sludge and organic fertilizer (CJ/T309-2009)

No.	Item	Standard	Sludge	Organic fertilizer	Soils
1	Organic matter (g/kg, dry basis)	≥200	397	490	18.25
2	Total nutrient ($N+P_2O_5+K_2O$) (%)	3	7.65	8.14	1.37
3	pH Value	5.5-9	7.5	8.4	7.98
4	Water content (%)	-	60	19.72	15.74
5	Mortality of roundworm eggs (%)	≥95	96.2	98.5	96.5
6	Fecal coliform population (g/per unit)	≥0.01	0.005	0.02	0.02
7	Total copper (Cu, mg/kg)	A level<500 B level<1500	183.71	190.52	44.83

Note: According to standard CJ/T309-2009, sludge of A and B are respectively used for different crops, A level is suitable for all crops, and B level is not suitable for vegetable and food crops.

2.2.3 Maize Cultivation

The cultivation experiment was conducted from May 20 to August 28, 2018, and the growing season was 100 days in total. The temperature and rainfall during this period are as follows: the average monthly maximum temperature is between 34 ℃ and 37 ℃, the average monthly minimum temperature is between 10 ℃ and 20 ℃, and the total rainfall during the experiment is 425 mm. A popular maize cultivar Zhengdan 958 was used for cultivation experiment of sludge. The cultivar is about 250 cm high, middle-late maturity, 96-125 growth days in Tianjin, and highly resistant or resistant to NLB, SCLB, head smut, MDMV, stem rot, lodging, and drought.

Five treatments were designed basing on the components of cultivation medium, and they were: CK, agricultural soil without addition; T1, agricultural soil with raw sludge; T2, agricultural soil treated with ozone sludge; T3, agricultural soil with ozone treated and electric treated sludge; T4, agricultural soil added with common organic fertilizer. Sludge amount used in every treatment was determined according to nitrogen requirement of maize growth, referencing TS=1%. Sludge was applied before maize sowing, jointing stage, and filling stages, and the total amount (60% water content) was 1.5 kg/pot (50 t/hm$^{2)}$. Five replications were arranged for each treatment at first, namely 25 pots in total.

Well-developed seeds were placed on vermiculite for seedling and then transplanted into pot at two-leaf stage. Pot is 59 L in volume (upper diameter is 44 cm, bottom diameter is 26 cm, and the height is 60 cm), and each holds 50 L of soil. Plant density was 8 plants/m2; soil moisture was kept at 70% of field capacity.

2.3 Maize Sample Collection and Analysis

At maturity, maize sample was collected from only three of five pots of a treatment, based on the growth situations. Plant height and stem length were measured. Cu content in plant parts and the upper(0-19cm), middle(20-39cm) and bottom(40-60cm) soil layers were investigated.

2.3.1 Sample Preparation

The collected plants were first washed by using ionized water, dried with ashless filter, and then divided into root, stem, ear, cob and seed parts and put into paper bags. Weight of these samples were achieved after they were fixed at 105℃ for 15 min and dried at 60℃ to constant weight (Muchow, 1994). Sample was ground into 0.2-mm pieces for Cu measurement. A 1.0000 g was digested using 5 mL HNO_3 for more than 12 h, then heated at 110℃ for 1.5 h in a Digestion System ED36 (USA), cooled and added into 1 mL H_2O_2, heated at 110℃again for 2.5 h, and then subjected to acid-dressing treatment till 1 mL solution left and finally diluted to 25 mL (Jamali, et al. 2013).

2.3.2 Preparation of Sludge and Soil Sample

Air dry the soil sample to be tested. Quartering was used for sampling. The sludge and soil samples were ground, and sifted using a 100-m sieve. Then a 0.1000 g sample was taken and put into a Digestion Tube, wetted by adding several drops of deionized water, added into 3 mL concentrated HCl and 1 mL concentrated HNO_3 and kept overnight in a fuming cupboard; the sample was then transferred to a Digestion System for digestion of 1 h at 80-90℃ and of 1 h at 120-130℃; after cooling, it was added into 1 mL of $HClO_4$ for further digestion of 0.5 h at 100-110℃and of 1 h at 20-130℃; after digestion finished, the sample was transferred into a volumetric flask for acid-dressing treatment and diluted to a constant volume of 25 mL at last.

2.3.3 Analysis Method

Cu was determined by the flame atomic absorption spectrometry (FAAS) (Jamali, et al. 1996) by TAS-990 Atomic Absorption Spectrophotometer. After microwave digestion, Cu amount in electric-treated sludge solution was determined by ICP-OES (Agilent 5110) and ICP-MS (Agilent 7700E).

2.4 Data Preparation and Analysis

Biological enrichment factor (BCF), also known as bioconcentration factor, is used to indicate the enrichment characteristics of an element in organisms. BCF of Cu was calculated according to the equation: BCF=Cp/Cs, where Cp was Cu content in the aboveground part of plant and Cs was the heavy metal content in soil. The value of BCF is over >1 means the element is enriched and has been influenced by human activities; the value of BCF is close to 1 indicates the element comes from crust weathering. Translocation factor is adopted to evaluate the capability of a plant transferring a certain element from root to aboveground parts, and it is calculated according to the equation: Translocation factor=Element content of aboveground part of a plant/Element content of roots of a plant. The higher the value of translocation factor is up to, the more the element is transferred to aboveground parts of a plant. The value of over 0.5 of an element indicates that the plant is capable of transferring most of the absorbed element by root to aboveground parts.

The single factor analysis of variance was use to analyze the measured data with software DPS16.05; the least significant different (LSD) was performed for multiple comparisons at 0.05 and 0.01 levels. Figures were plotted at Microsoft Excel 2016.

3. Results and Discussions

3.1 Effect of ozonation on Cu element

After centrifuged at 4 000 r /min, soluble supernatant (water phase) and insoluble precipitate (mud phase) can be separated from sample of sludge mixture. During ozonation process, the amount of Cu in mud phase increased at first and then decreased, while the Cu amount in water phase had been increasing gradually, with the fast increase rate occurred at 20 min after ozone aeration, but no Cu peak happened at 40 min after ozone aeration (Figure 1), indicating more Cu would be released from sludge later. The result indicated that ozone aeration affected the release of Cu from sludge and during the process Cu element was transformed into copper ions (Cu^{2+}) that were free in water phase.

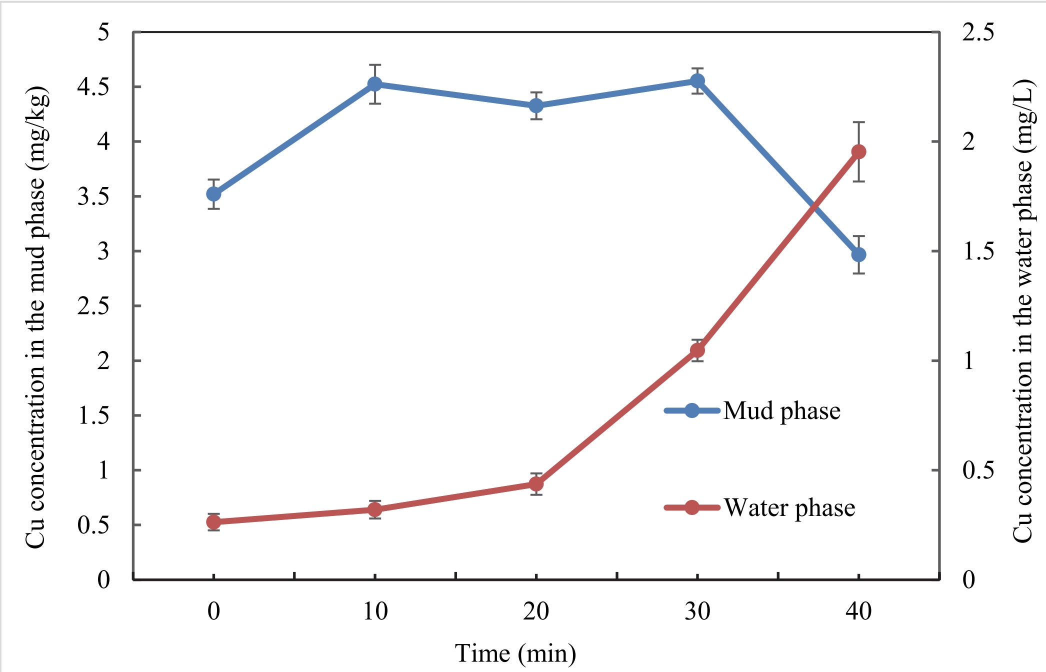

Figure 1. Effect of ozone oxidation on Cu in sludge

3.2 Removal Rate of Cu from Sludge

As shown in Figure 2, in electric field, Cu content in water phase showed a decrease trend with electric treatment going on, with the fastest rate occurred from starting to 10 min after electric treatment, but it almost unchanged during 10 to 120 min after electric treatment. As the main forms of Cu in sewage sludge was carbonate (6.27%), sulfide and organic combination substance (73.80%), and Cu residues (19.52%) and Cu element combined with organic substance and Cu residues were difficult to be separated from sludge by electric power, the removal percentage of Cu from sludge could not reach a high level (Yuan et al. 2006). Interestingly, Cu content in water phase increased again after 120 min of electric treatment, and the removal rate of Cu from sludge was increased too. The pheromone was due to a strong acidic environment formed in the cathode region at 120 min after electric treatment, promoting the removal of Cu^{2+}, and the lower the pH was the higher the removal rate would be (Liu et al. 2015), for at that time some organic complexing copper and metallic residues of Cu of sludge started to dissolve into water phase and then could be removed. At 240 min after electric treatment, the highest removal rate of Cu appeared, which was up to 27.87%. Except for the time points of 10 and 30 min after electric treatment, the differences between other time points were significant.

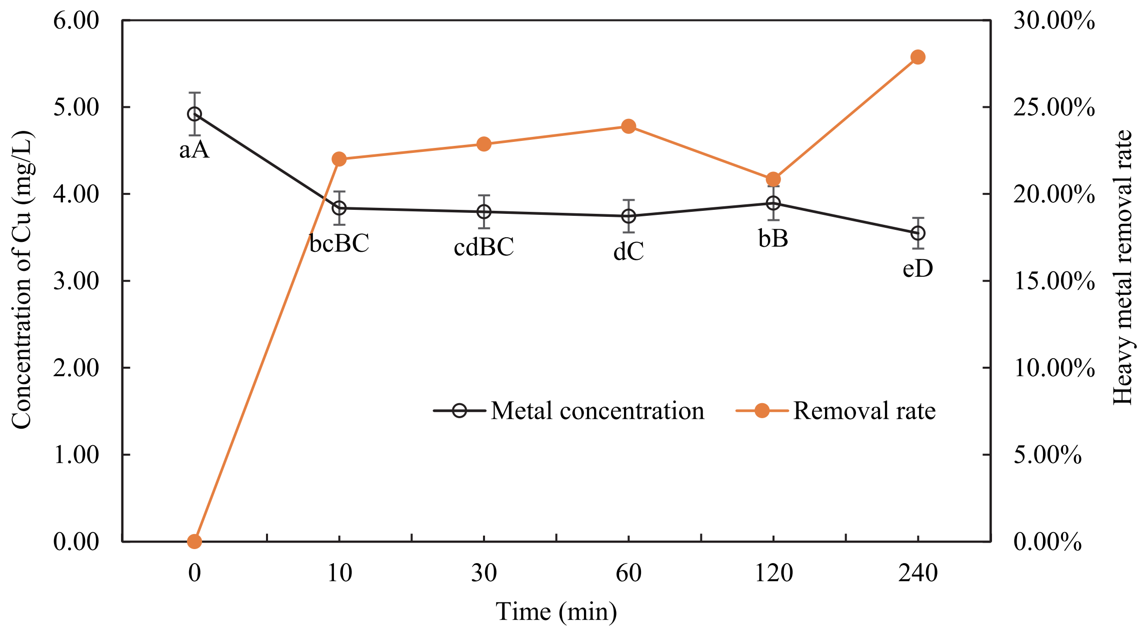

Figure 2. Removal rate of Cu in sludge mixture by electric power

3.3 Translocation of Cu in Plant

Cu content of every organs of maize were ranked as root>stem>leaf>cob>kernel in all treatments except for CK, in which the Cu content of maize organs was in the order of root >leaf>stem >cob>kernel (Figure 3). Namely, Cu content showed a decreased trend from bottom to up of a plant. Among five treatments, the highest Cu content (11.60 mg/kg) was found in plant root of T1, but there was no significant difference between treatments. This indicated that plant Cu content was influenced by soil Cu more or less, and both ozonation and electric treatment were capable of removing Cu from sludge, resulting less Cu accumulated in plants. The lowest Cu content (1.36 mg/kg) was in the kernels of CK, but there was no difference among treatment of CK and T1-T3 in Cu content of kernels; Cu contents of kernels of CK and T1-T3 was less than that of T4 (organic fertilizer applied). Sparks (1995) considered that Cu has strong adsorption capacity to organic and inorganic soil colloid and it is a kind of inactive metal. And in organic substances, copper is mainly bound to humic acid and fulvic acid, which are stable complexes. Mandal et al. Mandal (2000) found that the humic acid- fulvic acid chelate play a key role in absorbing Cu. It can be seen that the copper content in root system is the highest, but the difference is not significant in stem and leaf. The copper concentration in cob and grain decreases step by step compared with leaf, and the copper concentration in grain generally drops to less than 2mg/kg, indicating that the copper concentration in different organs is related to its absorption capacity and Cu transport capacity.

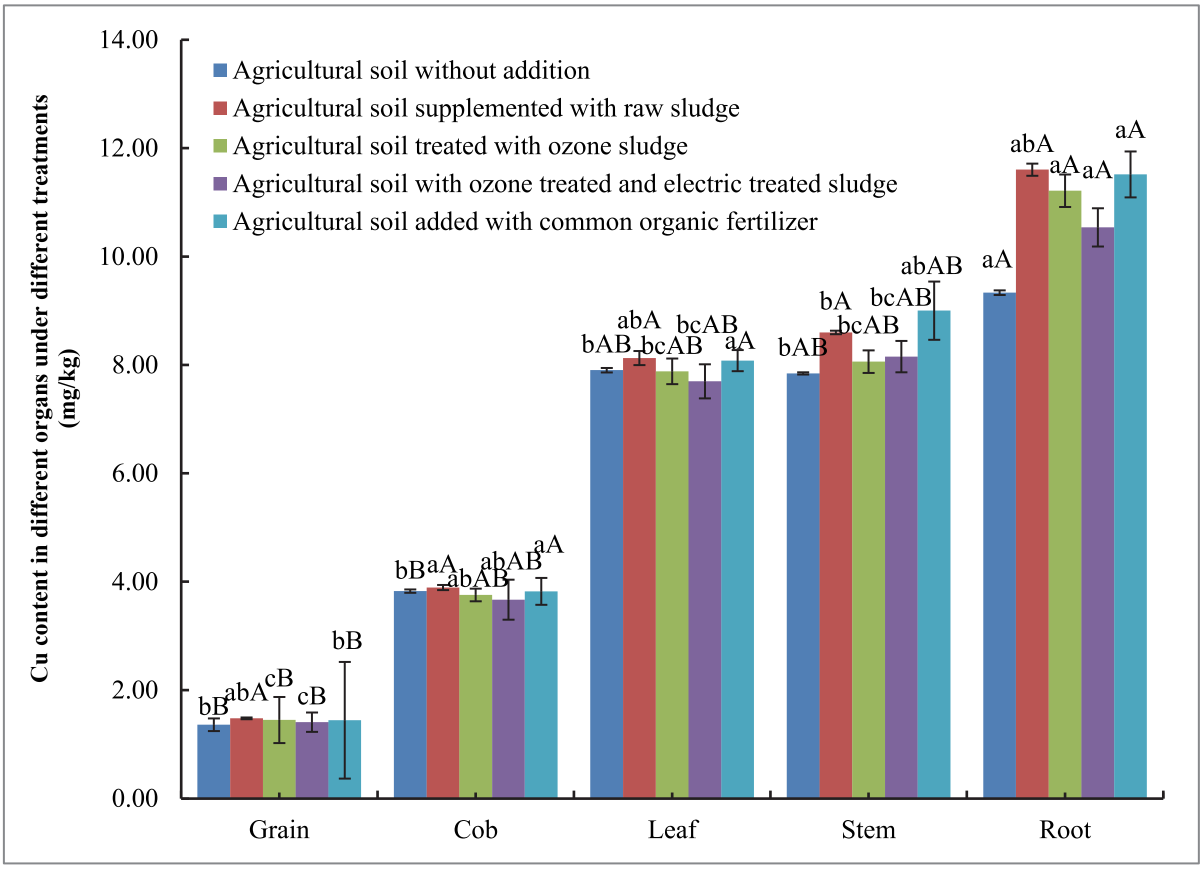

Figure 3. The content of metal Cu in different organs of maize

3.4 Distribution of Cu in Different Soil Layers

As shown in Figure 4, T4 and CK respectively had the highest and lowest Cu contents in every soil layers, and the difference between CK and T4 was significant. Three treatments of T1-T3 applied with sludge contained the middle level of Cu in every soil layers, and there was no significant different among them. According to Cu content in upper and bottom soil layers, the three treatments were ranked as T1＞T2＞T3, while based on Cu content of middle soil layer, the three treatments were in the order of T2＞T1＞T3, but there was no significant different between T1 and T2. Therefore, soil Cu was positively affected by both ozone treatment and ozone-electric treatment, and Cu content of sludge was lower than that of organic fertilizer. Cu content increased from upper to bottom soil layers but no statistic difference was found among soil layers in all treatments except CK. The result showed a small amount of Cu transferred from upper soil to bottom soil, and the Cu content of soil was mostly determined by the properties of soil itself.

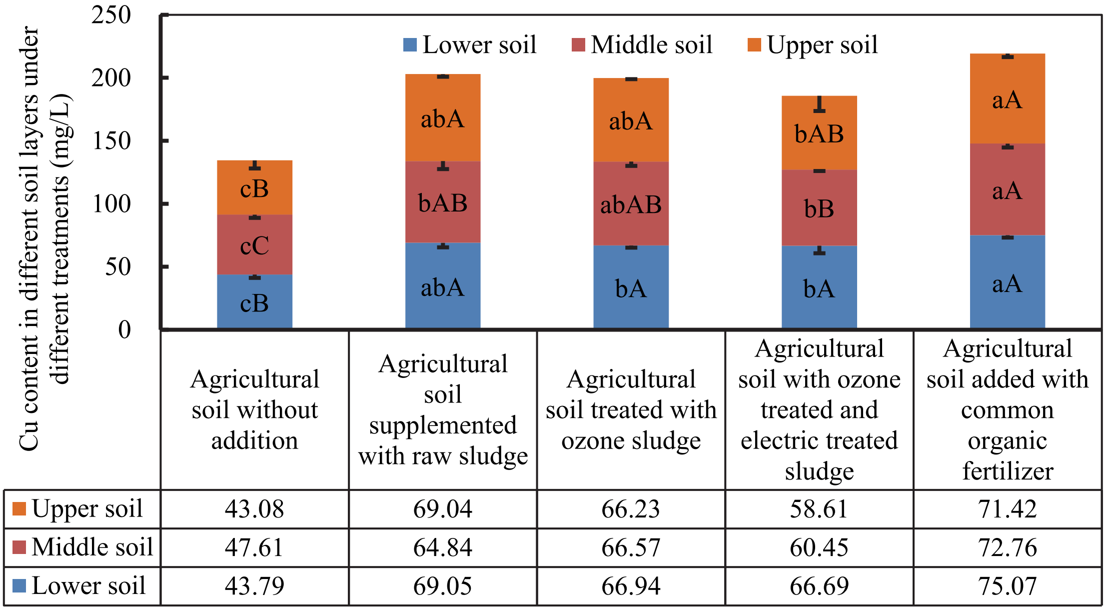

Figure 4. The content of metal Cu at every soil layer in different treatments

3.5 BCF of Cu of Various Organs in Every Soil Layer

Cu is one of the richest metals in maize plants (Udom et al. 2004). As can be seen from Table 3, the BFC were significantly different for various organs in every soil layer. The enrichment efficiency of Cu was higher in CK than in other treatments, but the BFCs of Cu of T1-T4 were similar. In upper soil layer, the BFC of cob, leaf, stem of CK was extremely significantly different from other treatments, and that of root and kernel of CK was significantly different from other treatments. In middle soil layer, the BFC of cob, leaf, stem and root of CK was extremely significantly different from other treatments, and that of kernel of CK was significantly different from other treatments. In bottom soil layer, BFC difference of all organs of CK was extremely significantly different from other treatments. The results indicated that enrichment efficiency of Cu was closely associated with soil Cu instead of fertilizer level, and ozone treatment only and the combination ozone and electric treatments did not alter enrichment efficiency of Cu in plants that was mainly determined by the property of plant itself.

Table 3. BCF of heavy metal Cu by various organs in every soil layer

Soil		Kernel	Cob	Leaf	Stem	Root
Upper layer	CK	0.03±0.01aA	0.09±0.01aA	0.19±0.03aA	0.19±0.03aA	0.22±0.04aA
	T1	0.02±0.00bA	0.06±0.00bB	0.12±0.00bB	0.12±0.00bB	0.17±0.01bA
	T2	0.02±0.00bA	0.06±0.00bB	0.12±0.00bB	0.12±0.01bB	0.17±0.01bA
	T3	0.02±0.01abA	0.06±0.01bB	0.14±0.03bAB	0.14±0.02bAB	0.19±0.05abA
	T4	0.02±0.00bA	0.05±0.00bB	0.11±0.00bB	0.13±0.01bB	0.16±0.01bA
Middle layer	CK	0.03±0.00aA	0.08±0.00aA	0.17±0.02aA	0.17±0.01aA	0.20±0.02aA
	T1	0.02±0.0abA	0.06±0.01bB	0.13±0.01bB	0.13±0.02bAB	0.18±0.02abAB
	T2	0.02±0.00bA	0.06±0.01bcB	0.12±0.00bB	0.12±0.01bB	0.17±0.01bAB
	T3	0.02±0.00bA	0.06±0.00bB	0.13±0.01bB	0.13±0.00bAB	0.17±0.01abAB
	T4	0.02±0.00bA	0.05±0.00cB	0.11±0.00bB	0.12±0.01bB	0.16±0.01bB
	CK	0.03±0.00aA	0.09±0.01aA	0.18±0.02aA	0.18±0.01aA	0.21±0.04aA
	T1	0.02±0.00bB	0.06±0.00bB	0.12±0.01bB	0.12±0.01bB	0.17±0.01bAB

Soil		Kernel	Cob	Leaf	Stem	Root
Bottom layer	T2	0.02±0.00bB	0.06±0.00bB	0.12±0.01bB	0.12±0.00bB	0.17±0.01bAB
	T3	0.02±0.00bB	0.06±0.01bB	0.12±0.01bB	0.12±0.01bB	0.16±0.02bAB
	T4	0.02±0.00bB	0.05±0.00bB	0.11±0.00bB	0.12±0.00bB	0.15±0.00bB

Note: The different lowercase and uppercase letters in a column indicate significant differences among treatments at P<0.05 and P<0.01 levels, respectively.

3.6 Translocation of Cu in Maize Plants

The transferring of Cu in maize plants is present in Figure 5. According to the transferring rate from root to stem, treatments were sorted as CK＞T3＞T4＞T1＞T2. Except for the difference between CK and T2 was significant, the other treatments were similar in the transferring rate from root to stem. This showed that insufficient fertilizer condition was favor of Cu transferring from root to stem of maize plant; CK was higher than T1-T4 in transferring rate of Cu; T4 (organic fertilizer treatment) showed a bit higher transferring rate than T1-T3 (sludge treatments), but there was no significant different among them. According to the transferring rate from root to leaf, the treatments were in the order of CK＞T3＞T4≈T1≈T2. That is, no fertilizer treatment (CK) presented higher transferring of Cu from root to stem than other treatments; electric treatment promoted the transferring of Cu; sludge without processed, sludge after treated by ozone, and organic fertilizer had not effect on the transferring rate of Cu from root to leaf (Figure 5).Based on Cu transferring from root to cob, the five treatments were ranked as CK＞T3＞T1＞T4≈T2. CK was significantly higher than all treatments except for T3 in the transferring rate. No fertilizer condition and sludge after treated with electric power both promoted Cu transferring from root to cob, but there was no significant difference between treatments with sufficient fertilizer. All treatments in the our experiment were similar in Cu transferring rate from root to kernel, namely the transferring rate of Cu from root to kernel of maize hardly affected by fertilizer types and levels. According to Cu accumulated in plant, the treatments were in the order of CK＞T3＞T4＞T1＞T2, indicating the accumulation of Cu in plants was closely related to fertilizer level and most of them concentrated in root, stem and leaf of maize plants.

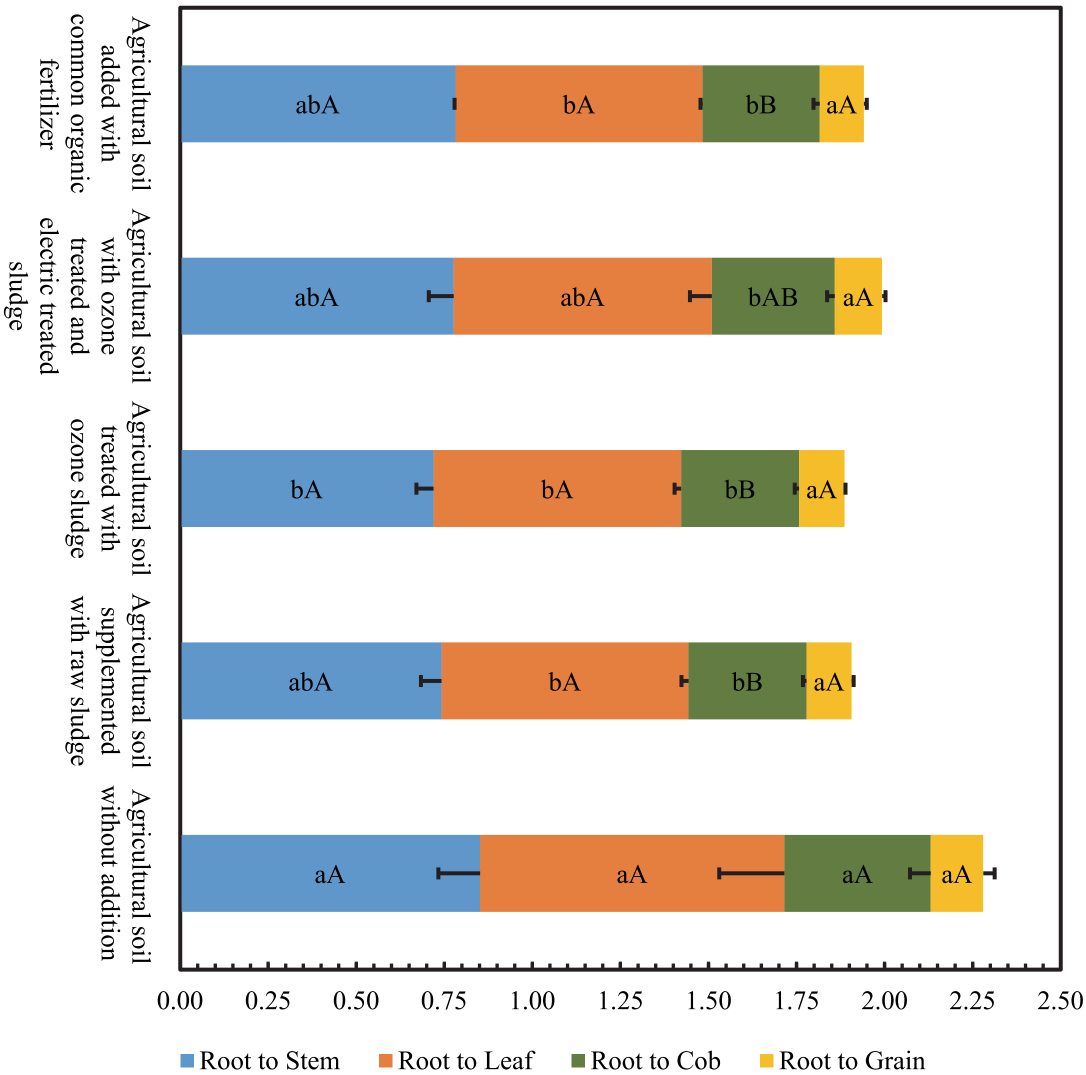

Figure 5. The transferring of Cu in plant in different treatment

Note. The abscissa represents the transfer rate

4. Conclusions

Ozone aeration is capable of breaking the wall of sludge particulates and then release copper from sludge quickly. The released Cu amount was positively correlated with the time length of ozone treatment, and 20-40 min of ozone treatment could achieve good result of Cu releasing, indicating there would be more Cu released from sludge when the mineralization process continued.

In 48 V direct current field, the removal rate of Cu was relatively stable during 10-120 min of electric treatment, ranging from 22% to 24%, and reached the maximum of 27.87% at 240 min. The lowest and highest Cu contents are found in maize kernel and root, respectively. With the increase of Cu content in soil, the Cu content of maize organs increased significantly. Compared to other treatments, every pretreatment step can reduce the Cu content of organs mentioned above.

Cu content showed an slight declined trend from bottom to top (from root to kernel) of maize, but Cu accumulation was not affected by the amount of sludge. Both sludge and organic fertilizer significantly increased Cu content of cultivation medium, and ozone-electric treatment reduced the Cu of sludge, but the Cu content in the grains did not change significantly. Therefore, the utilization of sludge as fertilizer did not significantly change the Cu content in maize. The Cu content in all treatments meets the standard of agricultural production. The pretreatment of sludge meets for the requirement of farmland fertilizer and ensures the safety of crop production. Compared with organic fertilizers, the use of sludge does not accumulate more Cu in soil.

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Authors' Contributions, Peng Yang: Data curation and analysis, Writing-Original draft preparation. Jiahua Liu: Sample collection, Sample pretreatment, Experimental analysis. Ruying Li: Project administration, Supervision. Chunyan Song: Supervision, Methodology, Writing-Reviewing and Editing.

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