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BIOLOGICAL PERFORMANCE OF CUPROUS AND CUPRIC COPPER AGAINST WOOD DECAY FUNGI

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BIOLOGICAL PERFORMANCE OF CUPROUS AND CUPRIC COPPER AGAINST WOOD DECAY FUNGI

By

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ABSTRACT

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Copper naphthenate and copper ethanolamine solutions with various copper metal concentrations (0 to 1%) were formulated and used to treat southern yellow pine and sugar maple. After treatment, a post-treatment steaming was conducted at various length of time, from 0 to 240 minutes. Atomic absorption spectrometer (AAS) was used to analyze the copper concentration in treating solutions and in treated wood.

A colorimetric method based on the specific reaction of cuprous copper (Cu (I)) and 2,2'-biquinoline in acetic acid matrix was used to monitor and to quantify Cu (I) in solutions and in treated wood. Data clearly indicate that the post-treatment steaming promotes the conversion of Cu (II) to Cu (I). This was confirmed by the increase of Cu (I) with the increase of the post-treatment steaming duration period.

A laboratory soil block test was conducted using both white and brown rot fungi. The decay index of copper naphthenate treated southern yellow pine and sugar maple, and copper ethanolamine treated sugar maple challenged by copper tolerant brown rot, *Poria placenta*, were significantly influenced by the content of Cu (I) / Cu (II). The weight loss was higher in treated wood with higher Cu (I) content, suggesting that the toxicity of Cu (I) to decay fungi is lower than that of Cu (II). It was hypothesized that Cu_2O is less toxic because it is less soluble in water, which blocks the further interactions between copper and fungi or wood components.

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INTRODUCTION

1.1 Background and proposed work

Wood bio-deterioration is generally caused by biological decay including fungi stains, insect infestation, etc. The properties mostly affected are the density and the mechanical properties.

The wood-destroying microorganisms are subdivided into four main groups: white rot, brown rot, soft rot, and mold/stain fungi (Eaton and Hale, 1993).

White and brown rot fungi are predominant agents of fungal degradation of wood. Their enzymatic capacities to depolymerize wood provide them with the potential to colonize wood at all stages of decomposition. Brown-rot fungi are mostly common in coniferous species, whereas white-rot fungi are frequent in angiosperms (Rayner and Boddy, 1988). Therefore, brown rot and white rot are the most frequently used fungi in study of wood protection.

Copper compounds have been used as fungicides over a century. Water-borne copper based preservatives such as ammoniacal copper arsenate (ACA), ammoniacal copper zinc arsenate (ACZA), acid copper chromate (ACC), chromated copper arsenate (CCA), copper bis (dimethyldithiocarbamate) (CDDC), ammoniacal copper citrate (CC), ammonical copper quat (ACQ-B and ACQ-D), copper azole-type A (CBA-A), and oil-borne copper based wood preservatives such as copper naphthenate, oxine copper (copper-8-quinolinate) are listed in American wood-preservers' association standards (AWPA, 1999).

Copper naphthenate (Cu-N) was introduced as a wood preservative in 1900. Cu-N is particularly effective against cellulose-destroying fungi and could afford long-lasting protection (Eaton and Hale, 1993). Freshly treated Cu-N products have a green / blue color and a strong odor that negatively impact their use (De Groot et al., 1988). To reduce the green color, the strong odor for environmental reasons, and to obtain a clean dried surface, Cu-N treated products are sometimes suggested to post-treatment steaming at 240°F (115°C) as recommended in the footnote of the AWPA book of standards (AWPA, 1996).

The reduction of Cu (II) to Cu (I) and the formation of cuprous oxide (Cu_2O) in post-treatment steamed Cu-N treated southern pine were reported by Kamdem and Zhang (1998). It is explained that the formation of Cu_2O is promoted by the carboxylic acids generated during the post-treatment steaming. These wood acids can protonate the naphthenate ligand of Cu-N into napthenate acid and the formation of copper carboxylate / acetate / formate / glucuronate / hydroxide. Under some specific conditions, the new form of copper may be transformed partially or totally into Cu_2O (Kamdem and Zhang, 1998). The fungicidal activities of copper-based compounds such as copper naphthenate, copper amine, copper-8-quinolinate may depend on the valence or the oxidation states of the copper in the treating solutions and in the treated wood. Little information is available in the literature about the toxicity of metallic copper, cuprous and cupric copper.

Copper amine system is one of the main ingredients of ACQ-D, CDDC, and copper azole. Its relatively low mammalian toxicity and environmental risk may help its

promotion as the preservatives in the future. Cu_2O can also be obtained from a copper-amine-treated wood after a post-treatment steaming, which is monitor in the lab by XRD.

This provides an interesting question about the bio-performance of wood containing Cu_2O. Could the post-treatment steaming promote the formation of Cu (I)? Is there any difference in the bio-performance between cupric copper and cuprous copper as wood preservatives?

Efforts have been invested in studying the mechanisms of copper toxicity to fungi (Hill, 1977). Mocquot et al. (1996) reported that the activities of certain enzymes are affected by the copper content in young maize. Gastaldi et al. (1993) reported that the cupric ion could inhibit the alcohol dehydrogenase 1 from *Kluyveromyces marxianus*. It is hypothesized that copper acts as a cofactor for electron donor and acceptor for many enzymatic reactions including oxidation, hydroxylation and dismutation. Excess of copper is reported to cause damage through oxidizing proteins and lipids and enhancing the toxic intra- and extra-cellular free radicals (Goyer and Cherian, 1995).

Superoxide radicals ($O_2^{\cdot-}$) and H_2O_2 are known to be produced in many biological systems, but these are relatively harmless as they react with bio-molecules at low rates. Simpson et al. (1988) suggested that in the presence of Cu (II) ion complexes, $O_2^{\cdot-}$ and H_2O_2 could lead to the formation of hydroxyl radical ($OH^{\cdot}$), which could damage the protein molecules in tissue. Similar reactions could take place in the presence of organic hydroperoxides (ROOH), Cu (II) could be reduced to Cu (I) resulting in the formation of peroxy ($ROO^{\cdot}$) radical and the more reactive alkoxy ($RO^{\cdot}$) radical (Hunt et al., 1988).

Little information is available about the biochemistry of copper and proteins under normal conditions (Hamer, 1986). The absorption / reaction sites of copper and

proteins are hypothesized to the carboxylic groups and the amino groups in the amino acids of the proteins. Therefore, the copper-oxygen and copper-nitrogen interactions may be determinant factors to the copper-fungi toxicity.

The objective of this work is to characterize Cu (I) and Cu (II), quantify Cu (I) and Cu (II) in treated wood and determine the biological performance of Cu (I) and Cu (II) in treated wood by challenging with laboratory pure culture of white and brown rot decay fungi.

LITERATURE REVIEW

It is important to understand the factors that affect the growth and development of fungi in wood substrates. Like all living organisms, fungi have certain requirements for growth and survival. The major growth needs of wood-inhabiting fungi are water, oxygen from air, a favorable temperature and a good food source. Fungi can digest wood to obtain energy and some compounds important for their metabolism (Zabel and Morrell, 1992). Decay fungi are clarified in three main groups: white rot, brown rot and soft rot decay fungi. The control of oxygen and temperature to reduce the decay process is a little difficult. Water can be limited by using dried wood. The hygroscopicity nature of wood can not limit the absorption of water by wood used in eternal application. One of the most effective ways of controlling decay is to put toxicants in the food source, which is wood.

2.1 White rot decay

White-rot fungi are known to degrade lignin. The degraded wood is white and soft. Most of the white-rot fungi prefer hardwoods. This may be due to the amount and the type of lignin (Schultz and Nicholas, 1997). The content of lignin in hardwood is about 18 to 25 % in dry weight and about 25 to 35 % in softwood (Haygreen and Bowyer, 1996). The building blocks for hardwood and softwood are shown in Figure 1. It is proposed that lignin in wood can act as antioxidant and disrupts various white-rot free radical degradative mechanisms (Schultz and Nicholas, 1997). An attack by white-

rot fungi causes a decrease of strength properties and an increase of swelling (Fengel and Wegener, 1983).

The most characteristic property of white-rot fungi is that they can produce ligninases. Staining and growth test of the fungal mycelium gave evidence of the presence of these enzymes (Paice and Jurasek, 1979; Schmidt and Liese, 1980). Lignin peroxidase was found in *Trametes versicolor* and other white rot fungi. It plays a key role in lignin degradation. *Trametes versicolor* requires H_2O_2 to oxidize and break the bond between carbons in phenyl propane units in lignin (Zabel and Morrell, 1992). From the elemental analysis of isolated lignin after fungal attack, the amount of oxygen is higher compared to that in the isolated lignin without fungal attack (Kirk, 1971; Kirk and Chang, 1974). The increase of oxygen in the lignin molecule derives from an oxidation of lignin.

The hyphae of white rot fungi penetrate the wood tissue through the pit membranes and through the cell walls by forming bore holes (Rayner and Boddy, 1988). At the macroscopic level, this leads to a remarkable honeycomb-like pattern of decay (Kirk, 1973). Species of white-rot fungi include *Trametes versicolor, Phanerochaete chrysosporium, Pleurotus ostreatus and Schizophyllum commune,* etc. (Eaton and Hale, 1993).

2.2 Brown rot decay

Brown-rot decay results in a selective degradation of cellulose and hemicellulose. Brown rot decay fungi can produce cellulase and hemicellulase, to digest or hydrolyze cellulose and hemicellulose. It is reported that the enzymatic degradation of cellulose is

influenced by the presence of monosaccharides, which act as a starter-substance or aid in the decomposition of the crystalline structure (Koenigs, 1974; Highley, 1976, 1977, 1980).

Chemical analysis of wood decayed by brown-rot fungi such as *Poria monticola*, *Lenzites trabea* and *Lentinus lepideus* shows a significant reduction of the polysaccharide content. The wood cellulose and polyoses undergo an extensive depolymerization before any significant weight loss is noticed (Kirk and Highley, 1973). The reduction of the mechanical properties at an earlier stage of decay is a good indication of brown rot decay. Lignin is also subjected to a limited degradation. UV spectrophotometric studies of brown rot decayed wood show a relative increase of the lignin content. This can be explained by the relatively larger amount of cellulose and hemicellulose depolymerized compared to that of lignin. X-ray diffraction study of cellulosic material treated with cellulase shows a reduction of the crystallite width of cellulose, indicating that attack by brown-rot fungi starts at the amorphous region of cellulose (Rayner and Boddy, 1988).

Brown-rot fungi are more frequent on softwood. The effect of lignin type and quantity on the rate of brown rot decay is considerably less than that recorded with white rot fungi (Schultz and Nicholas, 1997). Decayed wood becomes friable, ultimately powdery, and cracks cubically. The mechanical strength of wood is reduced. The hyphae of brown rot decay fungi grow mainly in the lumen of the wood cell walls (Wilcox, 1973). Abnormal longitudinal shrinkage and deformation of the cell walls is also observed (Fengel and Wegener, 1983).

Koenigs (1974) found that brown-rot fungi produce more H_2O_2 than the white-rot fungi, and suggested that the initial attack on crystalline cellulose by brown-rot fungi be

via a non-enzyme H_2O_2/Fe^{2+} system, which generates hydroxyl radical. Species of brown-rot fungi include *Coniophora puteana, Serpula lacrymans, Antrodia vaillantii, Gloeophyllum trabeum and Poria placenta*, etc. (Eaton and Hale, 1993).

2.3 Soft rot decay

Soft-rot is found both in softwoods and hardwoods, and results in various rates of reduction of the strength properties (Fengel and Wegener, 1983). Soft-rot fungi degrade cellulose and hemicellulose but do not appear to break down lignin appreciably (Rayner and Boddy, 1988). Soft-rot attack is typified by the formation of unique longitudinal bore holes in the secondary cell wall (Zabel and Morrell, 1992). The decay is characterized macroscopically by surface softness. Soft-rot fungi can produce cellulases and hemicellulases such as endo- and exo-1, 4-β-glucanases, β-glucosidases, which are capable of degrading cellulose and hemicellulose in wood (Eriksson and Wood, 1985). Species of soft-rot fungi include *Chaetomium globosum, Lecythophora hoffmannii, Monodictys putredinis* and *Humicola alopallonella*, etc. (Eaton and Hale, 1993).

2.4 Classification of wood degradation by wood decay fungi

Liese (1970) presented a classification of decay types to wood tissue in decreasing severity of cell-wall damage:

1. Simultaneous white-rot fungi attack all cell-wall constituents, essentially uniformly during all decay stages;
2. Sequential white-rot fungi attack all cell-wall constituents; the initial attack is selective for hemicellulose and lignin;

3. Brown-rot fungi primarily attack the cell-wall carbohydrates, leaving a modified lignin at the end of the decay process;
4. Soft-rot fungi preferentially attack cell-wall carbohydrates in the S2 layer of the secondary cell wall, forming longitudinal cavities or eroding the wood cell wall from lumen surface in hardwoods or the S2 in conifers.

2.5 Chemical properties of copper

Copper is the first element of Group IB in the periodic table. The most abundant oxidation states for copper are Cu (0), Cu (I) and Cu (II).

The relative stability of the Cu (I) and Cu (II) are indicated by the oxidation / reduction potential data presented in Figure 2 (Cotton and Wilkinson, 1988). In aqueous solution only low equilibrium concentrations of Cu (I) can exist compared to the concentration of Cu (II) unless Cu (I) is complexed. For an example, $Cu(NH_3)_2^+$, etc. The only copper compounds stable in water are the highly insoluble Cu_2O, Cu_2S and CuCl, etc. The water instability of Cu (I) compounds is due partly to the greater lattice and solvation energies and higher formation constants for Cu (II) compounds. Ionic Cu (I) derivatives are readily to be oxidized to Cu (II), which is much more stable. Further oxidation to Cu (III) is possible but more difficult. There are only a few Cu (III) complexes known (Cotton and Wilkinson, 1988).

Table 1 lists some copper complexes and their oxidation states (Cotton and Wilkinson, 1988).

Cu (I) is a d^{10} ion and it is diamagnetic. Cu (II) is a d^{9} ion and it is paramagnetic. Cu (II) can be detected using electron paramagnetic resonance (EPR). No paramagnetic signal is obtained from Cu (I).

The identification and quantification of the types and forms of copper is well established for liquid samples. Speciations of copper can be done on liquid samples using compleximetric titration, polarography and anodic stripping volametry (Zirinoode and Kounaves, 1980).

X-ray photoelectron spectroscopy (XPS) is routinely used to determine the atomic composition and the valence states present on the surface of solid sample. It provides information such as the binding energy, the chemical shift of photoelectrons and Auger electron, which is used to identify the correspondent atom and the oxidative states. It was reported to detect the cupric and cuprous copper in Cu-N treated wood (Kamdem and Zhang, 1999).

Cu (II) compounds have a specific color. This provides an opportunity to explore spectrophotometry as a means to identify and quantify the presence of Cu (I) and Cu (II) in liquid and solid. The color derives from one of the following three main possibilities: charge-transfer transitions, d $\rightarrow$ d transitions and intraligand-orbital transitions.

Most Cu (II) complexes have a blue or green color due to the d $\rightarrow$ d transition. Cu (II) has a specific absorption band in the 600 to 900 nm regions (Cotton and Wilkinson, 1988). Cu (0) is tough, soft, and ductile reddish metal. Little information is obtained describing the color of Cu (I) complexes. This might be due to the instability of Cu (I) complexes in aqueous solution.

MATERIALS AND METHODS

3.1 Wood preparation

3.1.1 Wood species and wood sizes

Defect-free kiln dried sapwood boards of southern yellow pine (SYP) and sugar maple (SM) were selected in the study. Cubes measuring 14 mm for SYP and 17 mm for SM were prepared from these boards and dried in at 40°C for 24 hours. The moisture content after dried in oven was 4 ± 1 percent. The densities of wood blocks were 32 pounds per cubic foot (pcf) for SYP and 36 pcf for SM.

3.1.2 Treating solutions

Cu-N and Cu-EA solutions with the copper strength in treating solutions ranging from 0.0, 0.25, 0.5 and 1.0 percent (w/w) were prepared for treatment.

3.1.2.1 Cu-Napthenate (Cu-N)

A stock solution of Cu-N containing 2 % elemental copper, received from ISK Biosciences Corporation, was diluted with toluene from J.T. Baker Inc. Naphthenic acid is distilled from crude oil and may contain C5 to C35 carboxylic acids (Dzidic et al., 1988).

3.1.2.2 Cu-Ethanolamine (Cu-EA)

Cu-EA was made by mixing copper hydroxide and monoethanolamine with ethanolamine to copper molar ratio of 4:1 at room temperature in order for copper complexed with ethanolamine completely. Copper hydroxide and ethanolamine were both obtained from Aldrich Chemical Co.

3.1.3 Wood treatment

A modified full cell process was used to pressure treat wood blocks. The treatment consists of two steps. During the first step, a cylinder measured 3 inches in diameter and 6 inches in length was used for the pressure treatment with Cu-N / Cu-EA solutions. An initial vacuum of about 84.6 kPa (25 inches of mercury) was pulled for 10 minutes prior to the injection of the treating solutions. A pressure level of 690 kPa (100 psi) was applied for 30 minutes. The extra solution was removed from the cylinder and then a final vacuum applied for 30 minutes.

The second step consisted of post-treatment steaming. The treated blocks were placed on a tray and air-dried at room temperature for 24 hours. Three hundred blocks of Cu-N or Cu-EA treated wood were divided into 6 groups. Every fifty blocks were post-treatment steamed at 240°F (115°C) in autoclave for 0, 20, 40, 60, 120 or 240 minutes, respectively. After post-treatment steaming, wood samples were dried at 40°C until the weight reached constant weight.

3.1.4 Sterilization of wood blocks

Wood samples were sterilized by ionizing radiation using Co-60 sources according to AWPA standard E 10-91 (AWPA, 1999). The wood blocks were sealed in polyethylene bags. Nitrogen was introduced in the bags to reduce the oxygen content and limit the oxidization. The envelopes were subjected to radiation at a level of 2.0 to 2.5 Mrad. Half of these treated wood blocks were used in soil block tests and the other half were used for analysis.

3.2 Copper analysis

3.2.1 Analysis of elemental copper content in wood

Analysis of elemental copper content in treated cubes was determined by atomic absorption spectroscopy (AAS) using Atomic Absorption Spectrophotometer Model: Perking Elmer 3110 according to AWPA Standard A11-93 (AWPA, 1999). The wood blocks were ground into sawdust. About 0.2 g of wood sawdust was oven dried at 105°C and weighted. Samples were acid digested with nitric acid and perchloric acid following the AWPA Standard A7-93 (AWPA, 1999). The solutions after digestion were diluted to around 10 ppm for AAS analysis. The working standard for AAS was at wavelength of 324.8 nm with hollow cathode lamp as light source and air-acetylene as flame.

3.2.2 Analysis of Cu (I) in wood

3.2.2.1 Characterization of Cu (I) by UV/VIS spectrophotometery

The 2,2'-biquinoline reagent was prepared at room temperature by dissolving about 0.25 g of 2,2'-biquinoline in 250 ml of glacial acetic acid. The chemicals were both obtained from Aldrich Chemical Co.

The spectrum for different copper species in 2,2'-biquinoline reagent were collected by scanning respective solutions from 450 nm to 1000 nm using ultraviolet / visible spectrophotometer. A Beckman DU640 B spectrophotometer with a 10-mm light path silica cuvette from Sigma was used. All UV/VIS scans were performed at a speed of 600 nm/min. Cu_2O mixed with Cu-N or Cu_2O mixed with Cu-EA were prepared by mixing Cu_2O with Cu-N or Cu-EA treating solutions in 2,2'-biquinoline reagent.

3.2.2.2 Quantification of Cu (I) -2,2'-biquinoline complex in solution

The Cu (I)-2,2'-biquinoline complex was prepared by dissolving Cu_2O in 2,2'-biquinoline reagent (0.004 mol/l). The concentration of Cu (I) ranged from 0 ppm to 100 ppm (0 to 0.0016 mol/l) was determined by AAS. The solutions were stored for 20 minutes before detecting the UV/VIS absorption at 540 nm, which is the wavelength of the maximum absorbance for Cu (I)-2,2'-biquinoline complex in glacial acetic acid.

3.2.2.3 Cu (I) content in treated wood

The wood was ground to pass through 40-mesh sieve and then dried at 40°C in oven for 24 hours. The moisture content of wood powder was 4 ± 1 percent.

About 25 ml of 2,2'-biquinoline reagent was used to extract about 0.1 g wood powder by ultrasonic extraction for 5 minutes using ultrasonator Model: ULTRA sonik 57X from Cole-Parmer Instrument Co. with nitrogen protection against air oxidization.

After centrifugation, the supernatant was used for UV/VIS analysis. The absorption of the solution was measured at 540 nm (Felsenfeld, 1960).

3.2.2.4 Mass balance of Cu (I) and Cu (II) analysis

After the ultrasonic extraction, the wood powder was washed with 3 ml of 2,2'-biquinoline reagent for 4 to 5 times until the filter liquor turned colorless. The solutions were collected for both Cu (I) analysis and AAS analysis for the elemental copper. The wood powder was analyzed by AAS to determine the amount of copper that remained in wood. The copper contents detected from these two steps were compared to the elemental copper content in treated wood.

3.3 Soil-block test of Cu-N and Cu-EA treated wood after post-treatment steaming

Wood cubes treated by 0.5 % in elemental copper (w/w) Cu-EA treating solution and 0.25 % in elemental copper (w/w) Cu-N treating solution were used in study the bio-performance of cupric and cuprous copper challenged by wood decay fungi.

Two brown rot fungi, *Poria placenta* (Pp) (Fr.) Cooke (Madison 698,ATCC 11538) and *Gloeophyllum trabeum* (Gt) (Pers ex. Fr.) Murr (Madison 617, ATCC 11539), two white rot fungi, *Trametes versicolor* (Tv) (L. ex Fr.) (FP-101664-Sp, ATCC 42462) and *Pleurotus ostreatus* (Po) (Jacq. Ex Fr.) Kummer (ATCC 32237) were used to evaluate the bio-performance of cupric and cuprous copper in wood cubes as described in AWPA Standard E10-91 (AWPA, 1999) with some slight modification.

Aspen cut in 3 by 28 by 34 mm ($1/8 \times 1^1/_8 \times 1^3/_8$ in.) blocks were used as feeder strips. About 3.5 ± 0.5 g of malt extract agar was poured on the surface of feeder strips and the blocks were sterilized in an autoclave before introducing the wood cubes.

The malt extract agar was prepared by dissolving 7.5 g Difco Bacto malt extract and 10.0 g and Difco Bacto-agar from Difco Laboratories in 500 ml distilled water by stirring and heating below 80°C until it became transparent (Wang and Zabel, 1990).

Boxes were inoculated with a monoculture of fungus and incubated until the feeder strip was covered. Five replica for each sample group were introduced. The soil boxes were kept in a growing room at the temperature of 76°F and relative humidity of 90 % during the test. After 16 weeks for brown-rot fungi exposure and 20 weeks for white-rot fungi exposure, the cubes were removed from the culture boxes, scraped clean to remove superficial mycelium and reconditioned in an oven at 40°C until the weight stabilized. The percentage of weight loss after exposure to pure monoculture of test

fungus was used as the index of decay. Wood blocks were introduced to soil boxes with no fungi to obtain the operational weight losses due to the process.

The average moisture content of a soil box was taken by comparing the weight of the culture medium to the dried culture medium. The soil boxes were randomly selected and the weight of dried culture medium was obtained by oven drying at 105°C until the weight reached constant.

3.4 Statistical analysis

The correlation between the copper species (Cu (I) and Cu (II)) and the weight losses obtained after a soil block test were evaluated by Spearman order correlation analysis. One way ANOVA and Tukey analysis were used to evaluate the overall effect of post-treatment steaming on the weight losses of Cu-N and Cu-EA treated wood. All pairwise multiple comparison were evaluated within different duration periods of post-treatment steamed wood to certain fungus exposure.

RESULTS AND DISCUSSION

4.1 Wood appearance

Cu-N treated wood has a green / blue color with a strong odor. Cu-EA treated wood has a blue color with no noticeable odor. The color changed to brown after post-treatment steaming and became darker with the increase of post-treatment steaming duration period for both Cu-N and Cu-EA treated wood.

4.2 Copper retention in treated wood

The copper retentions were achieved in mg/g: 1.88, 3.44 and 5.31 mg/g for Cu-N treated SYP, 3.13, 5.00 and 10.31 mg/g for Cu-EA treated SYP, 1.39, 2.50 and 4.17 mg/g for Cu-N treated SM and 2.50, 4.44 and 7.50 for Cu-EA treated SM in elemental copper (Tables 2 and 3). The copper retention after pressure treatment for SYP was higher than that of SM for the same treatment. The copper retentions in wood increase with the increase of the concentration of copper in the treating solutions as shown in Figures 3 and 4.

4.3 Cu (I) analysis in wood

Little research has been reported to estimate the Cu (I) content in treated wood quantitatively. Kamdem and Zhang (1998) used X-ray diffraction photoelectron spectroscopy (XRD) and (1999) X-ray photoelectron spectroscopy (XPS) successively to detect the Cu (I) in wood. Klotz and Klotz (1955) used a colorimetric reagent namely

2,2'-biquinoline in glacial acetic acid to determining the concentration of cuprous copper in *Busycon* hemocyanin. This method has been applied to determine the concentration of Cu (I) in protein chemistry, notably for the tyrosinase enzyme (Felsenfeld, 1960). The reaction scheme between Cu (I) and 2,2'-biquinoline is presented in Figure 5.

4.3.1 Characterization of Cu (I) - 2,2' - biquinoline by UV/VIS spectrophotometer

Cu (I) reacts with 2,2'-biquinoline in glacial acetic acid matrix yielding a pink color solution. Such color is not noticeable with cupric copper. The 2,2'-biquinoline reagent was colorless with pH value ranged around 2 ± 0.5. It takes about 20 minutes for the pink color to develop at room temperature. The pink color results from the solubilization of cuprous oxide and the formation of a Cu (I) complex with 2,2'-biquinoline (Kertesz, 1957).

Figure 6 presents the UV/VIS spectrum of Cu_2O, Cu-N, Cu_2O mixed with Cu-N in 2,2'-biquinoline reagent. An absorption band with λmax at 540nm was observed from Cu_2O dissolved in 2,2'-biquinoline reagent in spectra (c). The band was attributed to the new complex formed between Cu_2O and 2,2'-biquinoline. This maximum absorbance at 540 nm remained stable in presence of Cu-N as shown in spectra (a). There is no absorbance from Cu-N dissolved in 2,2'-biquinoline reagent at 540 nm in spectra (b).

Figure 7 presents the UV/VIS spectrum of Cu_2O, Cu-EA, Cu_2O mixed with Cu-EA in 2,2'-biquinoline reagent. The maximum absorbance for Cu (I)- 2,2'-biquinoline complex at 540 nm remained stable in presence of Cu-EA as shown in spectra (a). There is no absorbance from Cu-EA dissolved in 2,2'-biquinoline reagent at 540 nm in spectra (b).

The absorbance band for Cu-N and Cu-EA in 2,2'-biquinoline reagent were broadened when the concentrations of Cu-N and Cu-EA were decreased. These attributed to that Cu-N and Cu-EA were destroyed in acetic acid and Cu (II) - acetate was formed in acetic acid matrix (Zyskowski and Kamdem, 1999).

These results agreed with the conclusion from Klotz and Klotz (1955) that 2,2'-biquinoline react with cuprous copper to form a stable complex. Therefore, 2,2'-biquinoline was used to complex Cu (I) and the complex was quantified as the cuprous copper.

4.3.2 Quantification of Cu (I) -2,2'-biquinoline complex in solution

A calibration curve was constructed for cuprous concentration and the Cu (I)-2,2'-biquinoline complex in solution. Known amount of cuprous oxide was diluted with 2,2'-biquinoline reagent. A linear regression of $Y = (X-0.681)/6.885$ with R^2 value of 0.991 was obtained between the copper concentration determined by AAS and the UV/VIS absorbance between 4 and 10 ppm of elemental copper (Figure 8). X is the concentration of cuprous ion in ppm and Y is the UV/VIS absorbance at 540 nm. This regression line assumed that all Cu (I) in the solution was complexed with 2,2'-biquinoline and the intensity of absorbance was proportional to the amount of complex formed.

4.3.3 Cu (I) and Cu (II) content in treated Wood

About 7.9 % of the 1.88 mg/g elemental copper in Cu-N treated SYP was determined to be in the form of Cu (I). The content of Cu (I) increased to 37.0 % after 20 minutes of post-treatment steaming. Cu (I) content increased to 53.2 % after 60 minutes. The Cu (I) content was 55.6 % after 120 minutes and 51.9 % after 240 minutes (Table 2).

The Cu (I) content increased with the increasing of the post-treatment steaming duration period. The formation of Cu (I) increased sharply during the first 60 minutes of post-treatment steaming and reached a plateau after 60 minutes. This confirms the XRD and XPS finding reported by Kamdem and Zhang (1998, 1999). The equations presenting the Cu (I) content related to the post-treatment steaming time are listed in Figures 9, 10, 11 and 12. The equations were obtained from the every mean value of three replicas. Y represents the Cu (I) content (%) in form of elemental copper in wood, and X represents the post-treatment duration periods in minutes. Cuprous copper was detected from Cu-N and Cu-EA treated wood without post-treatment steaming as well. Nearly 10 ± 5 % of Cu (I) in terms of elemental copper was detected. The Cu (I) contents in untreated wood were 0.1 % for SYP and 0.1 % for SM and less than 0.1 % in treating solutions. This suggests that the Cu (I) detected came from the vacuum pressure treatment or drying in oven at 40°C. The equations reflected the Cu (I) detected with 0 minute of post-treatment steaming.

There was a slight decrease of Cu (I) content observed after 240 minutes of post-treatment steaming compared to the Cu (I) content after 120 minutes of post-treatment steaming in most specimens. The reason of this decrease was not clear. But it can be theorized that solid deposit of copper in the surface was lost during the sample preparation. Similar trends were observed for both Cu-N and Cu-EA treated wood with different copper retentions.

Figures 13, 14, 15 and 16 present the initial Cu (II) content and the Cu (II) content after post-treatment steaming. The Cu (II) contents in both Cu-N and Cu-EA treated SYP

and SM after post-treatment steaming increase with the increase of initial Cu (II) contents in wood, and decrease with the increase of post-treatment steaming time.

4.4 Mass balance for Cu (I) and Cu (II) analysis

The first column of Table 4 contains the value of Cu (I) determined by UV/VIS for several specimens. The second column represents the data of the AAS analysis of elemental copper content in ultrasonic extracts. The third column represents the data of elemental copper remained in solid wood sawdust after the extraction. The forth column is the copper content in specimens determined by AAS after vacuum pressure treatment with no extrication. Data obtained from the AAS analysis of elemental copper content in ultrasonic extracts and in wood sawdust after ultrasonic extraction were compared to the elemental copper content in wood with no extraction. About 96 to 106 % of copper was detected. About 64 % of copper was extracted after the ultrasonic extraction by comparing the elemental copper content in extracts and the elemental copper content in wood with no extraction. About 79 % of copper in extracts was determined as Cu (I) by comparing the UV/VIS analysis of Cu (I) content in extracts and the AAS analysis of elemental copper content in extracts. This suggests that some Cu (II) was extracted by 2,2'- biquinoline reagent during the ultrasonic extraction.

4.5 Soil block test

The moisture content in the soil substrate in boxes was 130 ± 5 %.

The average weight losses in percentage after fungi exposure and the descriptive statistics analysis for the standard deviation are listed in Tables 5 and 6 and Figures 17 to 20.

One way ANOVA analysis and Tukey test listed in Tables 8 to 11 present the overall effect of post-treatment steaming on the weight losses of copper treated wood.

4.5.1 Cu-N treated SYP after *Poria placenta* exposure

The average weight loss was 1.1 % for Cu-N treated SYP with 0 minute of post-treatment steaming after *Poria placenta* exposure. The weight loss increased to 24.2 % after 120 minutes of post-treatment steaming. The weight loss for untreated control was 56.9 %. There was a significant difference observed between wood samples groups of 0 minutes and 120 minutes of post-treatment steaming; and 0 minutes and 240 minutes; and 20 minutes and 240 minutes (Table 8 and Figure 17). No significant difference was observed among other sample groups.

4.5.2 Cu-N treated SYP after *Gloeophyllum trabeum* exposure

The average weight loss was 2.4 % for Cu-N treated SYP with 0 minute of post-treatment steaming after *Gloeophyllum trabeum* exposure. The weight loss increased to 9.0 % after 60 minutes of post-treatment steaming. The weight loss for untreated control was 40.0 %. There was a significant difference observed between wood samples groups of 40 minutes and 120 minutes of post-treatment steaming (Table 8 and Figure 17). No significant difference was observed among other sample groups.

4.5.3 Cu-N treated SM after *Poria placenta* exposure

The average weight loss was 14.2 % for Cu-N treated SM with 0 minute of post-treatment steaming after *Poria placenta* exposure. The weight loss increased to 35.4 %

after 40 minutes of post-treatment steaming. The weight loss for untreated control was 58.2 %. There was a significant difference observed between wood samples groups of 0 minutes and 40 minutes of post-treatment steaming; and 0 minutes and 60 minutes; and 0 minutes and 120 minutes; and 0 minutes and 240 minutes; and 20 minutes and 40 minutes; and 20 minutes and 60 minutes; and 20 minutes and 120 minutes; and 20 minutes and 240 minutes (Table 10 and Figure 18). No significant difference was observed among other sample groups.

4.5.4 Cu-N treated SM after *Gloeophyllum trabeum* exposure

The average weight loss was 0.4 % for Cu-N treated SM with 0 minute of post-treatment steaming after *Gloeophyllum trabeum* exposure. The weight loss increased to 4.6 % after 60 minutes of post-treatment steaming. The weight loss for untreated control was 66.3 %. There was a significant difference observed between wood samples groups of 0 minutes and 60 minutes of post-treatment steaming; and 0 minutes and 120 minutes; and 20 minutes and 60 minutes; and 20 minutes and 120 minutes (Table 10 and Figure 18). No significant difference was observed among other sample groups.

4.5.5 Cu-EA treated SYP after *Poria placenta* exposure

The average weight loss was 32.1 % for Cu-N treated SM with 0 minute of post-treatment steaming after *Poria placenta* exposure. The weight loss increased to 56.4 % after 20 minutes of post-treatment steaming. The weight loss for untreated control was 56.9 %. There was no significant difference observed among wood samples groups (Table 9 and Figure 19).

4.5.6 Cu-EA treated SYP after *Gloeophyllum trabeum* exposure

The average weight loss was 4.8 % for Cu-N treated SM with 0 minute of post-treatment steaming after *Gloeophyllum trabeum* exposure. The weight loss increased to 9.0 % after 60 minutes of post-treatment steaming. The weight loss for untreated control was 40.0 %. There was a significant difference observed between wood samples groups of 0 minutes and 60 minutes of post-treatment steaming; and 0 minutes and 120 minutes; and 0 minutes and 240 minutes; and 20 minutes and 60 minutes; and 20 minutes and 120 minutes; and 20 minutes and 240 minutes; and 40 minutes and 60 minutes; and 40 minutes and 120 minutes; and 40 minutes and 240 minutes (Table 9 and Figure 19). No significant difference was observed among other sample groups.

4.5.7 Cu-EA treated SM after *Poria placenta* exposure

The average weight loss was 50.2 % for Cu-EA treated SM with 0 minute of post-treatment steaming after *Poria placenta* exposure. There is a slight increase of weight losses observed with the increase of post-treatment steaming time. The weight loss for untreated control was 58.2 %. There was no significant difference observed among wood samples groups (Table 11 and Figure 20).

4.5.8 Cu-EA treated SM after *Gloeophyllum trabeum* exposure

The average weight loss was 0.7 % for Cu-EA treated SM with 0 minute of post-treatment steaming after *Gloeophyllum trabeum* exposure. There is a slight increase of weight losses observed with the increase of post-treatment steaming time. The weight loss for untreated control was 66.3 %. There was no significant difference observed among wood sample groups (Table 11 and Figure 20).

4.6 The weight losses and the copper content in wood

Figures 21 to 24 suggest that the average weight losses of Cu-N treated SYP and SM increased with the percentage of Cu (I) in wood exposed to *Poria placenta*. The relation between the weight losses and the Cu (I) content is not clear in Cu-EA treated wood after *Poria placenta* exposure. There was a slight variation but no significant difference in weight losses observed in most wood blocks exposed to *Gloeophyllum trabeum, Trametes versicolor* and *Pleurotus ostreatus*. The weight loss is relatively lower for samples exposed to *Gleophyllum trabeum, Trametes versicolor* and *Pleurotus ostreatus* compared to the specimens exposed to *Poria Placenta*. The increment of weight losses from 0 minute of post-treatment steaming to 240 minutes was no more than 10 % compared to the increment of 25 ± 5 % for the specimens exposed to *Poria Placenta*. This is attributed to the good performance of copper-based wood preservatives to most wood decay fungi (Zabel and Morrell, 1992). However, *Poria placenta* is a copper tolerant fungus (Sutter et al., 1983). The copper tolerance of *Poria placenta* is reported in both laboratory experiments and in service situation (Schimidt and Liese, 1996; Da Costan and Kerruish, 1964; Williams and Fox, 1994; Collett, 1992; Thornton and Tighe, 1987). This explained the relatively high weight losses obtained from both Cu-N and Cu-EA treated wood exposed to *Poria placenta* and the relatively lower weight loss exposed to *Gloeophyllum trabeum*, *Trametes versicolor* and *Pleurotus ostreatus* in this test.

Statistic analysis using Spearman rank order correlation presented the correlation coefficient for the Cu (I) or Cu (II) contents in wood and the weight losses after soil block test as shown in Table 7. A high correlation coefficient (more than 0.8) with low P value (less than 0.05) were observed in Cu-N treated SYP, Cu-N treated SM and Cu-EA treated

SM after *Poria placenta* exposure. The weight losses increased with the increase of Cu (I) content and decreased with the increase of Cu (II) content in wood samples.

No significant correlation was observed between the copper species and the weight losses for most specimens after *Gloeophyllum trabeum*, *Trametes versicolor* and *Pleurotus ostreatus* exposure.

Marten and Leach (1994) reported that the toxicity of Cu_2O toward *Pythium debaryanum* depends on its solubility in different conditions. Cu_2O is less toxic because it is less soluble in certain solution, which leads to less susceptible to interact with the wood decay fungi such as the amino acid functional groups. Comparing the data obtained from soil block test to the data obtained from copper analysis, we suggest that the toxicity of Cu-N treated SYP and SM, and Cu-EA treated SM towards wood brown rot decay fungi *Poria placenta* is attributed to the Cu (II) in wood in this post-steaming treatment.

CONCLUSIONS

Cuprous copper content in presence of Cu (II) in treated wood could be determined by the 2,2'-biquinoline method for Cu-N and Cu-EA treated SYP and SM after post-treatment steaming.

Based on the analysis of Cu (I) and Cu (II) content in treated wood and the data of soil block tests, Cu (II) can be converted to Cu (I) by using post-treatment steaming. The conversion ratio increases with the increase of post-treatment steaming duration period in the first 60 minutes for Cu-N and Cu-EA treated SYP cubes measuring 14 mm and SM cubes measuring 17 mm of copper retention ranged from 1.88 mg/g to 10.31 mg/g.

The weight losses of Cu-N and Cu-EA treated wood increase with the increasing of post-treatment steaming duration period in *Poria placenta*. The weight losses increase with the decrease of Cu (II) content, while the total copper retention remains the same.

In conclusion, Cu_2O in Cu-N treated SYP and SM and Cu-EA treated SM to *Poria placenta* is less toxic than Cu (II) in post-steaming treated wood.

Table 1. Oxidation States and Stereochemistry of Copper

Oxidation state	Coordination number	Geometry	Examples
Cu (I), d^{10}	2	Linear	Cu_2O, $CuCl_2^-$
	3	Planar	$K[Cu(CN)_2]$
	4[a]	Tetrahedral	CuI, $[Cu(CN)_4]^{3-}$
	4	Distorted planar	CuL[c]
	5	*sp*	$[CuLCO]^+$
	6	Octahedral	$\{(Ph_2MeP)_3ReH_5\}_2Cu$
Cu (II), d^9	3	Trigonal planar	$Cu_2(\mu\text{-}Br)_2Br$
	4[a,b]	Tetrahedral (distorted)	(N-Isopropylsalicylaldininato)$_2$Cu $Cs_2(CuCl_4)$
	4[a,b]	Square	CuO, $(NH_4)_2[CuCl]_4$
	6[a,b]	Distorted octahedral	$CuCl_2$
	5	*tbp*	$[CuCl_5]^{2-}$
	5	*sp*	$[Cu(NH_3)_5]^{2+}$ [d]
	6	Octahedral	$K_2Pb[Cu(NO_2)_6]$
	7	Pentagonal bipyramidal	$[Cu(H_2O)_2(dps)]^{2+}$ [e]
	8	Distorted dodecahedron	$Ca[Cu(CO_2Me)_4]\cdot 6H_2O$
Cu (III), d^8	4	Square	$KCuO_2$
	6	Octahedral	K_3CuF_6

[a] Most common states.
[b] These three cases are often not sharply distinguished.
[c] L= a macrocyclic N_4 anionic ligand.
[d] In $KCu(NH_3)_5(PF_6)_3$
[e] dps= 2,6-diacetylpyridine bis(semicarbazone)

Table 2. Cu (I) content in Cu-N treated wood after various periods of post-treatment steaming

Duration of post-treatment steaming (min)	Wood Species					
	SYP			SM		
	Copper Retention (mg/g)					
	1.88	3.44	5.31	1.39	2.50	4.17
	Cuprous Copper (mg/g)					
0	0.15	0.40	0.51	0.11	0.38	0.43
20	0.70	0.82	0.88	0.55	0.82	0.73
40	0.86	1.25	1.46	0.78	1.10	1.29
60	1.00	1.45	1.70	0.67	1.31	1.44
120	1.05	1.56	2.33	0.80	1.35	1.58
240	0.98	1.51	1.83	0.73	1.58	1.59

Table 3. Cu (I) content in Cu-EA treated wood after various periods of post-treatment steaming

Duration of post-treatment steaming (min)	Wood Species					
	SYP			SM		
	Copper Retention (mg/g)					
	3.13	5.00	10.31	2.50	4.44	7.50
	Cuprous Copper (mg/g)					
0	0.28	0.35	0.52	0.37	0.27	0.57
20	0.62	0.67	0.89	0.64	1.12	0.95
40	0.72	2.23	1.58	0.81	1.68	1.19
60	0.81	2.69	2.10	0.98	1.84	1.87
120	0.84	2.56	2.19	0.74	1.95	2.09
240	0.83	2.47	3.02	0.83	1.90	1.68

Table 4. Mass balance for Cu (I) and Cu (II) analysis

	UV/VIS extracts Cu^a (mg/g)	AAS extracts Cu^b(mg/g)	AAS extracted wood sawdust Cu^c (mg/g)	AAS treated wood Cu^d (mg/g)	Mass balance(%)
Cu-N SM 40	0.77	0.85	0.49	1.37	97.8
Cu-N SYP 240	0.78	1.00	0.56	1.62	96.3
Cu-N SM 240	0.72	1.06	0.40	1.37	106.6
Cu-EA SM 240	1.71	2.31	1.52	3.98	96.2
Cu-EA SYP 60	2.59	3.02	1.98	4.83	103.5
Cu-EA SYP 240	2.38	3.11	1.80	4.83	101.7

Cu^a: Cu (I) content (mg/g) in extracts after ultrasonic extraction obtained from UV/VIS analysis
Cu^b: Cu content (mg/g) obtained from AAS analysis of extracts after ultrasonic extraction
Cu^c: Cu content in wood sawdust after ultrasonic extraction using AAS analysis
Cu^d: Cu content in wood without extraction using AAS analysis

Table 5. Weight losses of SYP after laboratory soil block test

Treatment	Wood weight loss (%)*				
	Pp	Gt	Po	Tv	No fungus
Cu-EA 0min	32.1(7.7)	4.8(1.3)	5.4(1.5)	8.1(1.0)	0.3(0.2)
Cu-EA 20min	56.4(13.2)	6.8(1.0)	5.8(1.7)	11.2(2.1)	
Cu-EA 40min	47.9(18.3)	11.5(3.3)	13.8(2.2)	11.0(1.2)	
Cu-EA 60min	49.1(18.3)	9.0(0.9)	11.2(0.7)	11.7(2.2)	
Cu-EA 120min	51.4(10.7)	10.9(1.9)	11.3(0.8)	11.5(2.6)	
Cu-EA 240min	50.4(16.3)	11.0(1.5)	13.3(2.5)	12.5(1.6)	
Cu-N 0min	1.1(1.1)	2.4(2.6)	5.6(2.2)	5.4(2.9)	
Cu-N 20min	6.2(2.4)	2.2(2.4)	4.2(1.2)	5.6(1.6)	
Cu-N 40min	15.1(1.2)	2.0(3.6)	6.0(2.3)	6.3(2.0)	
Cu-N 60min	22.8(2.1)	6.8(2.5)	8.7(2.5)	10.4(1.2)	
Cu-N 120min	24.2(5.3)	7.5(2.3)	7.1(0.9)	11.6(2.1)	
Cu-N 240min	29.2(9.3)	5.6(3.2)	10.6(0.9)	12.1(2.4)	
Untreated	56.9(1.6)	40.0(18.1)	22.4(1.1)	22.0(2.1)	

* Values represent the means of five replicas. Values in parenthesis represent one standard deviation.

Table 6. Weight losses of SM after laboratory soil block test

Treatment	Wood weight loss (%)*				
	Pp	Gt	Po	Tv	No fungus
Cu-EA 0min	50.2(3.3)	0.7(0.8)	8.8(2.5)	8.2(1.6)	0.3(0.2)
Cu-EA 20min	53.2(5.5)	1.8(0.8)	6.3(2.5)	6.0(1.7)	
Cu-EA 40min	54.7(3.4)	1.4(1.4)	5.3(1.5)	5.5(1.5)	
Cu-EA 60min	56.6(3.3)	1.6(0.3)	5.5(1.9)	6.0(1.5)	
Cu-EA 120min	57.2(4.6)	1.1(0.5)	6.8(3.3)	6.2(3.0)	
Cu-EA 240min	56.2(5.0)	1.9(0.8)	5.5(1.1)	5.9(1.5)	
Cu-N 0min	14.2(2.8)	0.4(0.5)	-0.1(1.6)	0.2(0.5)	
Cu-N 20min	25.9(3.5)	1.9(1.1)	0.3(0.7)	0.2(0.4)	
Cu-N 40min	35.4(9.6)	2.6(1.2)	0.5(0.7)	0.3(0.7)	
Cu-N 60min	32.6(8.7)	4.6(2.0)	0.5(0.8)	0(1.1)	
Cu-N 120min	36.9(10.0)	4.5(1.5)	0.2(1.0)	0.4(0.6)	
Cu-N 240min	34.3(6.8)	2.9(1.3)	0.2(0.8)	0.4(1.3)	
Untreated	58.2(5.1)	66.3(7.3)	16.2(0.3)	19.1(1.34)	

* Values represent the means of five replicas. Values in parenthesis represent one standard deviation.

Table 7. Spearman rank order correlation for copper species and average weight losses after soil block test

Copper species	WL (Pp)	WL (Gt)	WL (Po)	WL (Tv)
	Cu-N treated SYP			
Cu (I) content	[a]0.829 [b]0.0583 [c]6	0.486 0.356 6	0.714 0.136 6	0.829 0.0583 6
Cu (II) content	-0.829 0.0583 6	-0.486 0.356 6	-0.714 0.136 6	-0.829 0.0583 6
	Cu-EA treated SYP			
Cu (I) content	0.257 0.658 6	0.714 0.136 6	0.429 0.419 6	0.771 0.103 6
Cu (II) content	-0.257 0.658 6	-0.714 0.136 6	-0.429 0.419 6	-0.771 0.103 6
	Cu-N treated SM			
Cu (I) content	1.000 0.00278 6	0.600 0.242 6	0.265 0.564 6	0.706 0.136 6
Cu (II) content	-1.000 0.00278 6	-0.600 0.242 6	-0.265 0.564 6	-0.706 0.136 6
	Cu-EA treated SM			
Cu (I) content	0.943 0.0167 6	0.257 0.658 6	-0.232 0.658 6	-0.232 0.658 6
Cu (II) content	0.943 0.0167 6	0.257 0.658 6	-0.232 0.658 6	-0.232 0.658 6

[a]:Correlation coefficient; [b]: P value; [c]: Number of samples

Table 8. Overall effect of post-treatment steaming on Cu-N treated SYP: weight losses from soil block test: Statistical One way ANOVA and Tukey

Pp		Gt	
0min	a	40min	a
20min	a c	20min	a b
40min	a d	0min	a b
60min	a e	240min	a b
120min	b c d e	60min	a b
240min	b d e	120min	b

* Data in column are ranked increasingly representing the mean value of weight losses after a soil block test with post-treatment steaming.
* Post-treatment duration periods followed by the same letter represent no significant difference in weight losses observed.
* Cu retention: 1.88 mg/g

Table 9. Overall effect of post-treatment steaming on Cu-EA treated SYP: weight loss from soil block test: Statistical One Way ANOVA and Tukey

Pp		Gt	
0min	a	0min	a
40min	a	20min	a
60min	a	60min	b
120min	a	120min	b
20min	a	240min	b
240min	a	40min	a

* Data in column are ranked increasingly representing the mean value of weight losses after a soil block test with post-treatment steaming.
* Post-treatment duration periods followed by the same letter represent no significant difference in weight losses observed.
* Cu retention: 5.00 mg/g

Table 10. Overall effect of post-treatment steaming on Cu-N treated SM: weight loss from soil block test: Statistical One Way ANOVA and Tukey

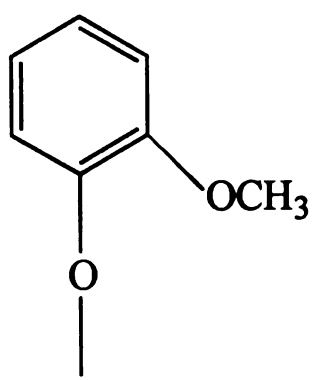
Pp		Gt	
0min	a	0min	a
20min	a	20min	a
60min	b	40min	a c d
240min	b	240min	a b
40min	b	120min	b d
120min	b	60min	b c

* Data in column are ranked increasingly representing the mean value of weight losses after a soil block test with post-treatment steaming.
* Post-treatment duration periods followed by the same letter represent no significant difference in weight losses observed.
* Cu retention: 1.39 mg/g

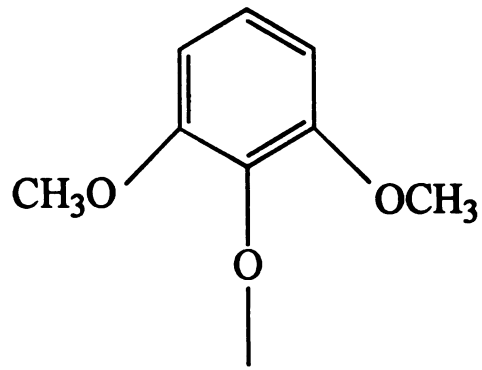
Table 11. Overall effect of post-treatment steaming on Cu-EA treated SM: weight loss from soil block test: Statistical One way ANOVA and Tukey

Pp		Gt	
0min	a	0min	a
20min	a	120min	a
40min	a	40min	a
60min	a	60min	a
240min	a	20min	a
120min	a	240min	a

* Data in column are ranked increasingly representing the mean value of weight losses after a soil block test with post-treatment steaming.
* Post-treatment duration periods followed by the same letter represent no significant difference in weight losses observed.
* Cu retention: 4.44 mg/g



Softwoods and hardwoods



Hardwoods

Figure 1. Building blocks of lignin (Haygreen and Bowyer, 1996)

$$Cu^{+} + e = Cu \qquad E^{0} = 0.52v$$

$$Cu^{2+} + e = Cu^{+} \qquad E^{0} = 0.153v$$

$$Cu + Cu^{2+} = 2\,Cu^{+} \qquad E^{0} = -0.37v$$

$$K = [Cu^{2+}] / [Cu^{+}]^{2} = \sim 10^{6}$$

Figure 2. Oxidation/reduction potential data of Cu (I) and Cu (II) (Cotton and Wilkinson, 1988)

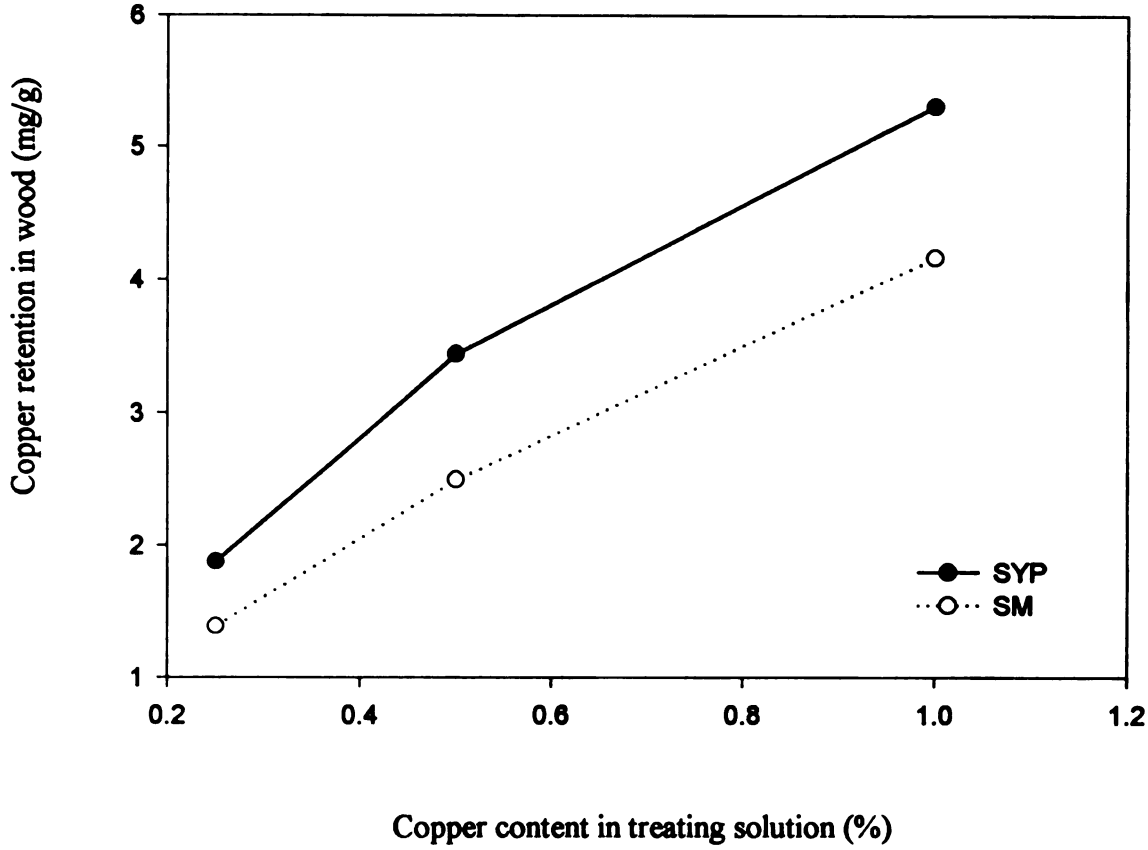


Figure 3. Copper retention in wood after pressure treatment with Cu-N

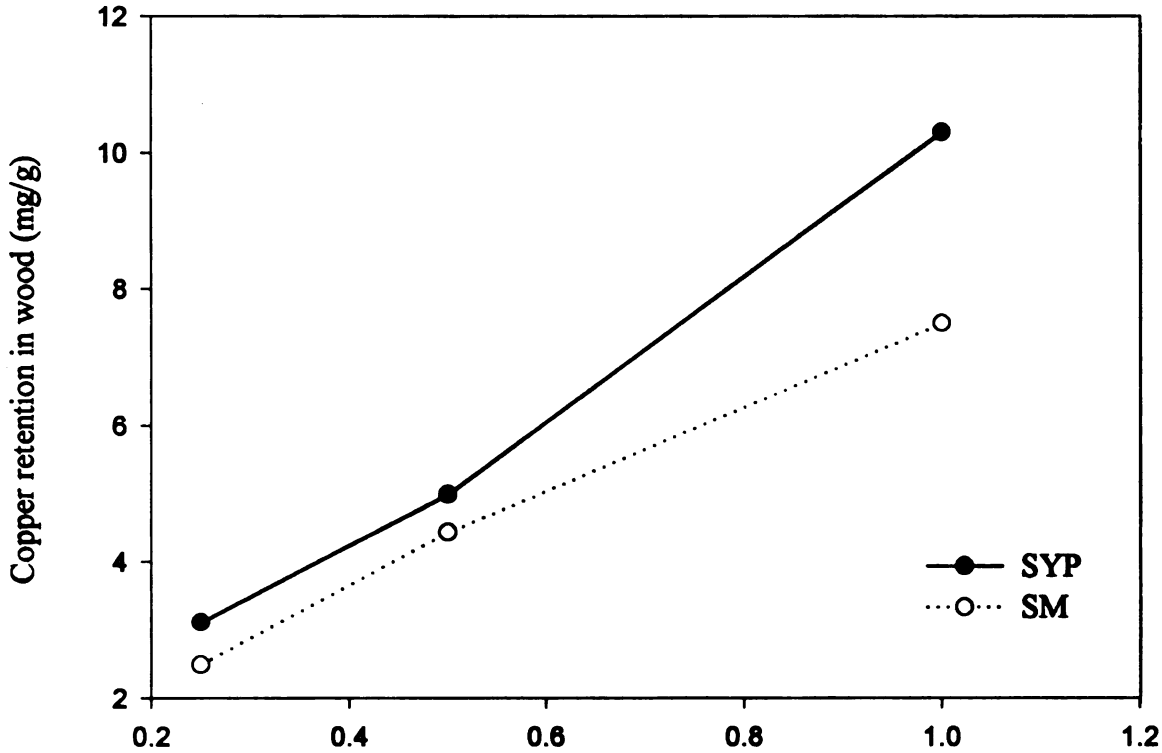


Figure 4. Copper retention in wood after pressure treatment with Cu-EA

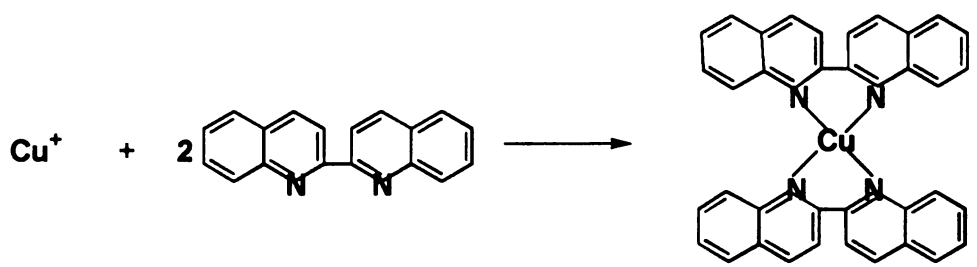


Figure 5. Cu (I) analysis using 2,2'-biquinoline (Deon et al., 1969)

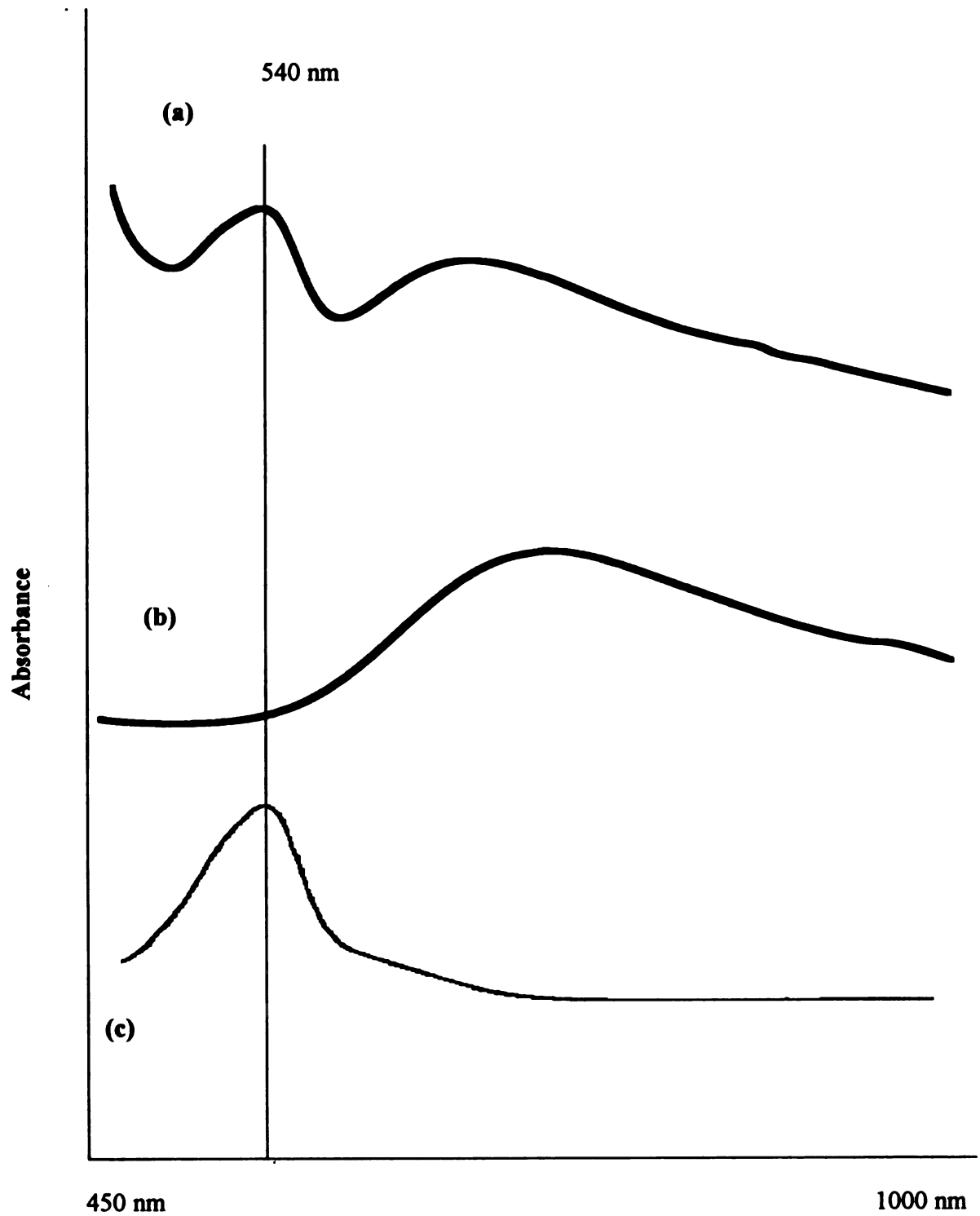


Figure 6. UV/VIS spectrum of (a) Cu_2O and Cu-N with 2,2'-biquinoline (b) Cu-N with 2,2'-biquinoline (c) Cu_2O with 2, 2'-biquinoline

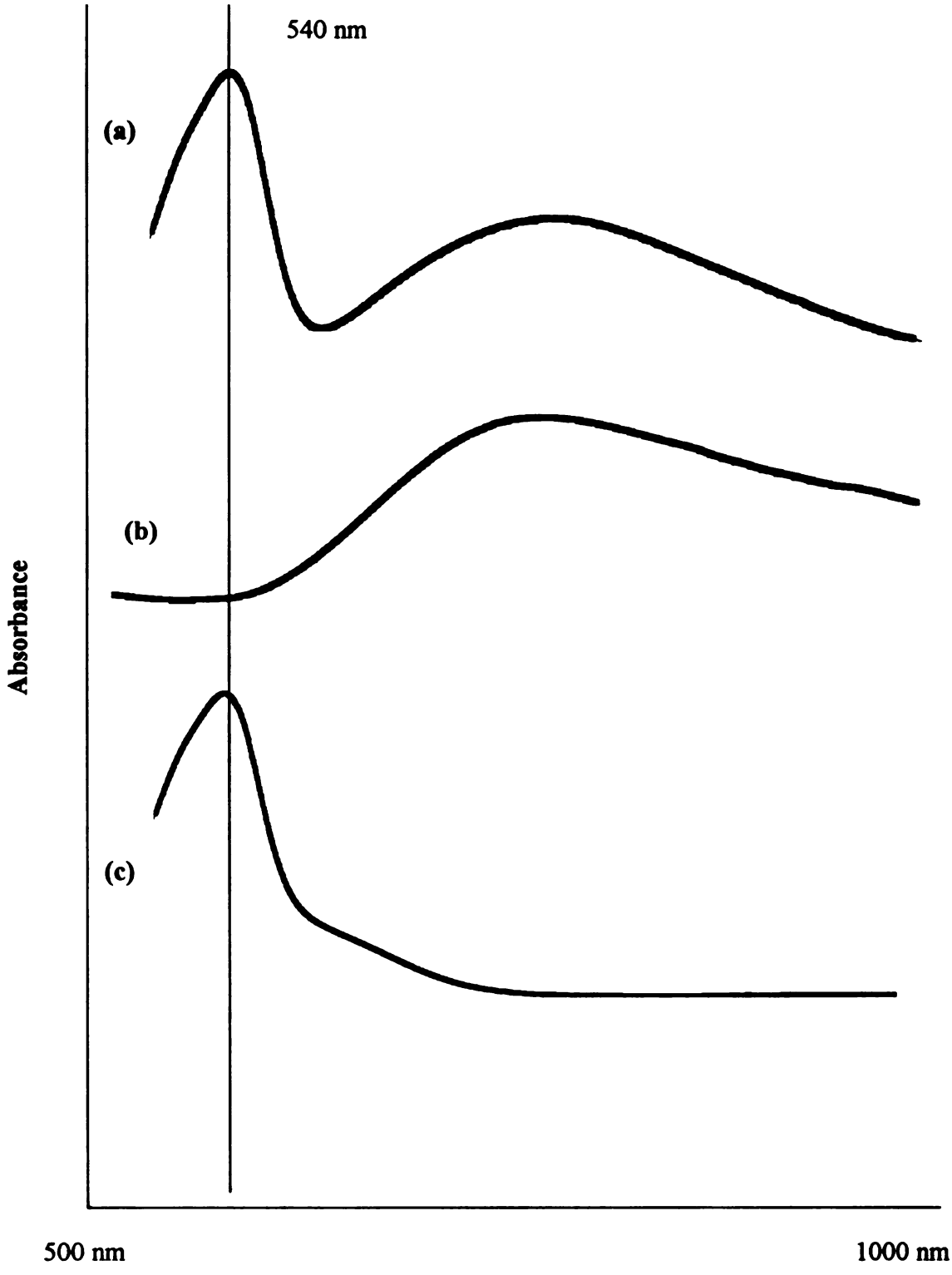


Figure 7. UV/VIS spectrum of (a) Cu_2O and Cu-EA with 2,2'-biquinoline (b) Cu-EA with 2,2'-biquinoline (c) Cu_2O with 2,2'-biquinoline

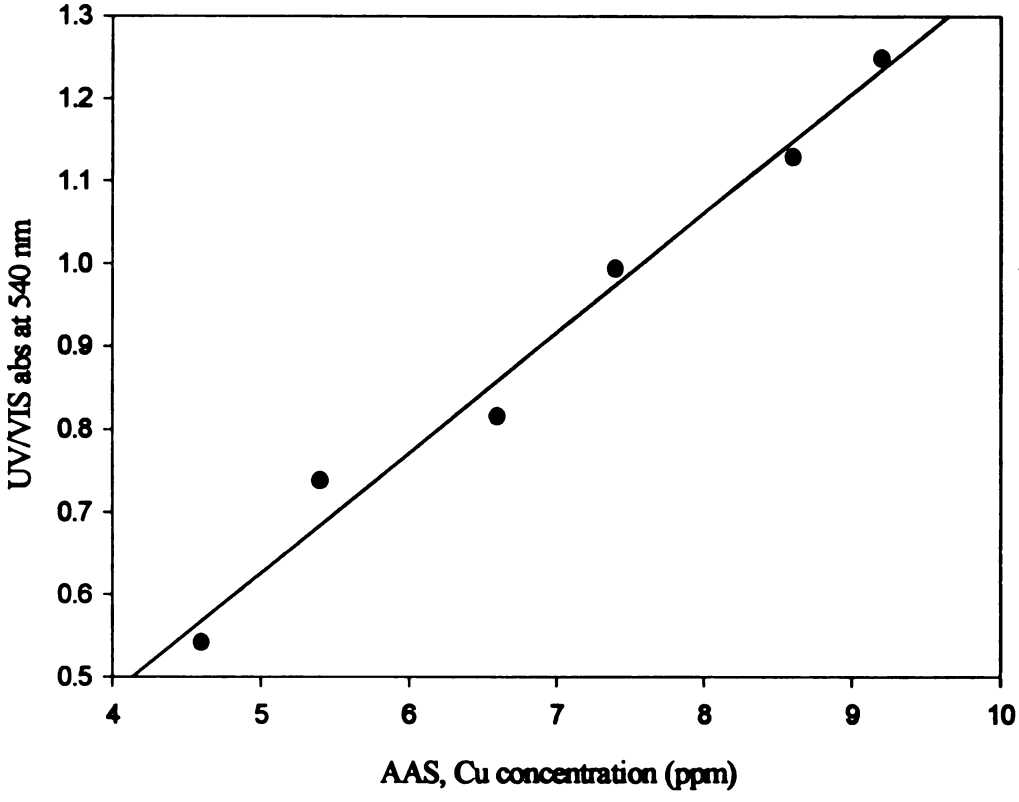


Figure 8. Calibration curve of Cu (I) -2,2'-biquinoline

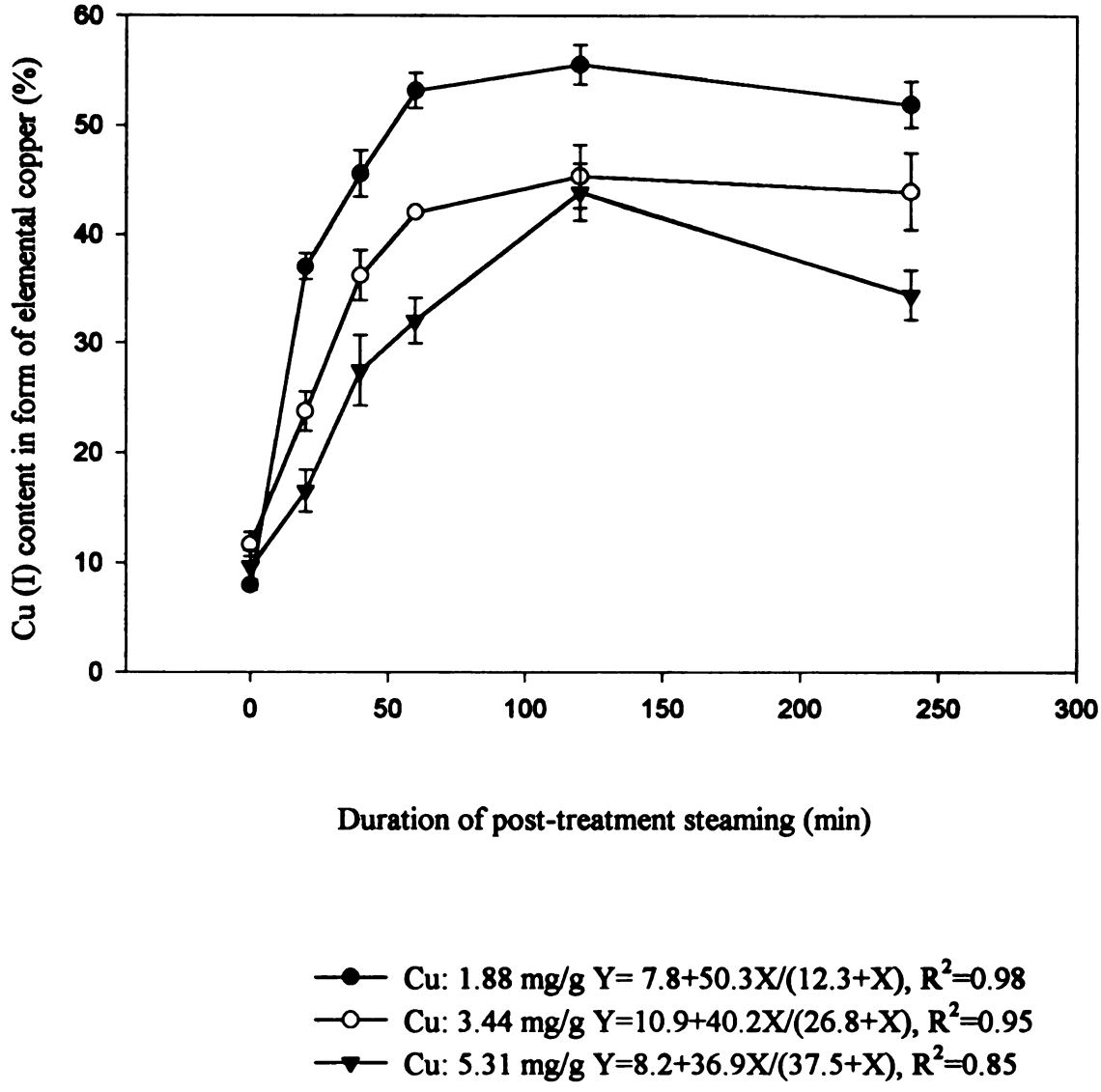


Figure 9. Cu (I) content in Cu-N treated SYP after post-treatment steaming

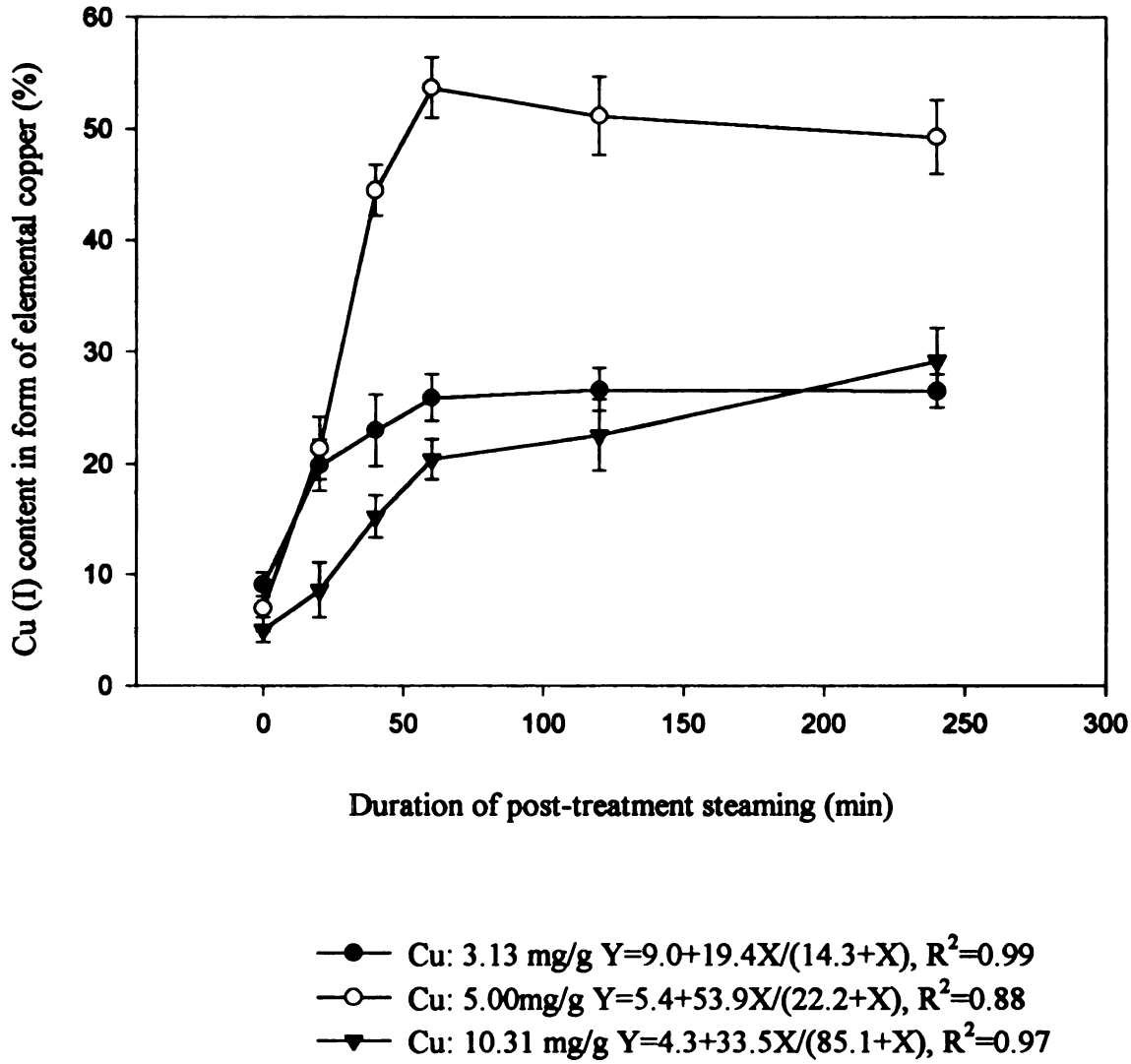


Figure 10. Cu (I) content in Cu-EA treated SYP after post-treatment steaming

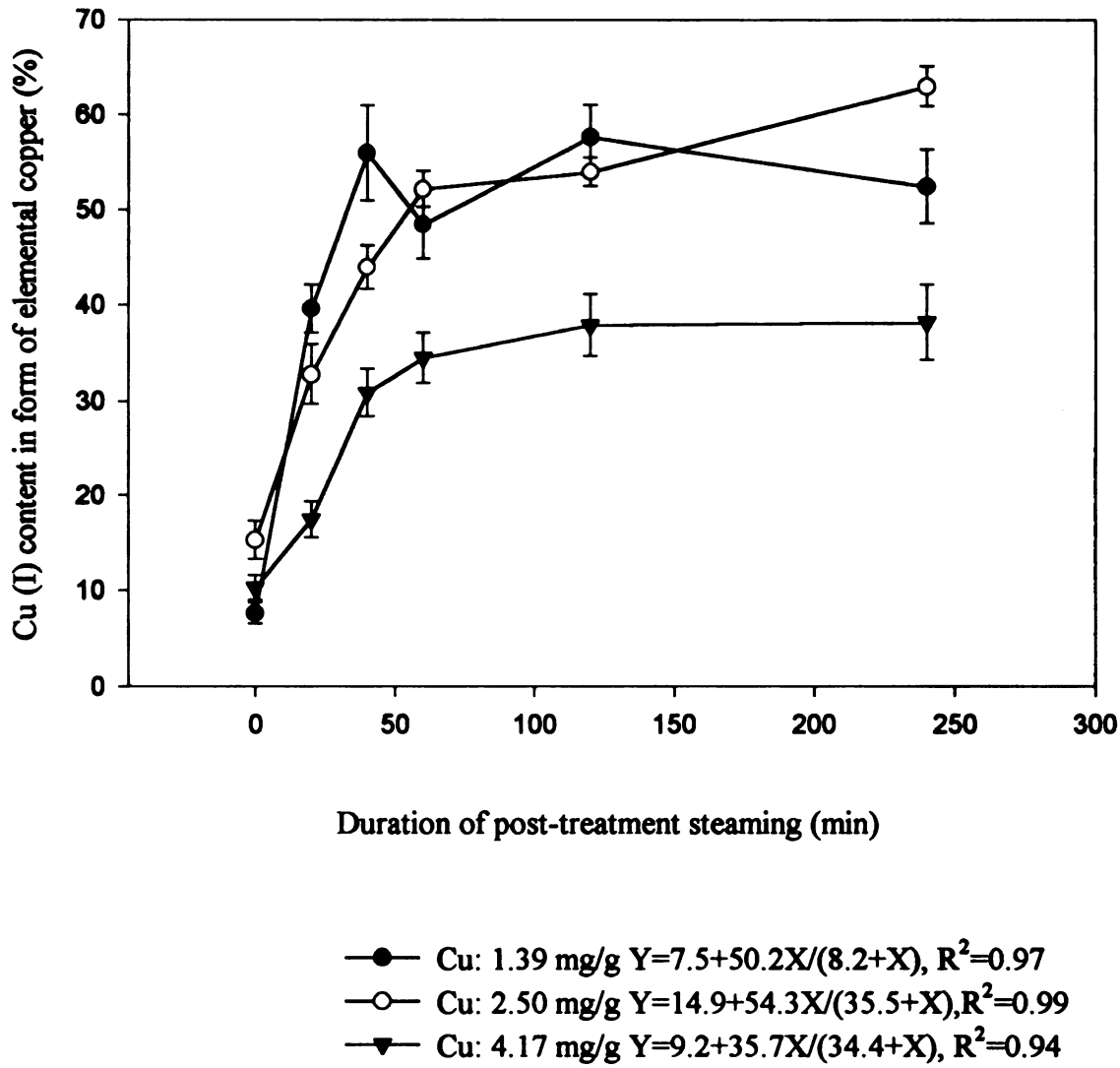


Figure 11. Cu (I) content in Cu-N treated SM after post-treatment steaming

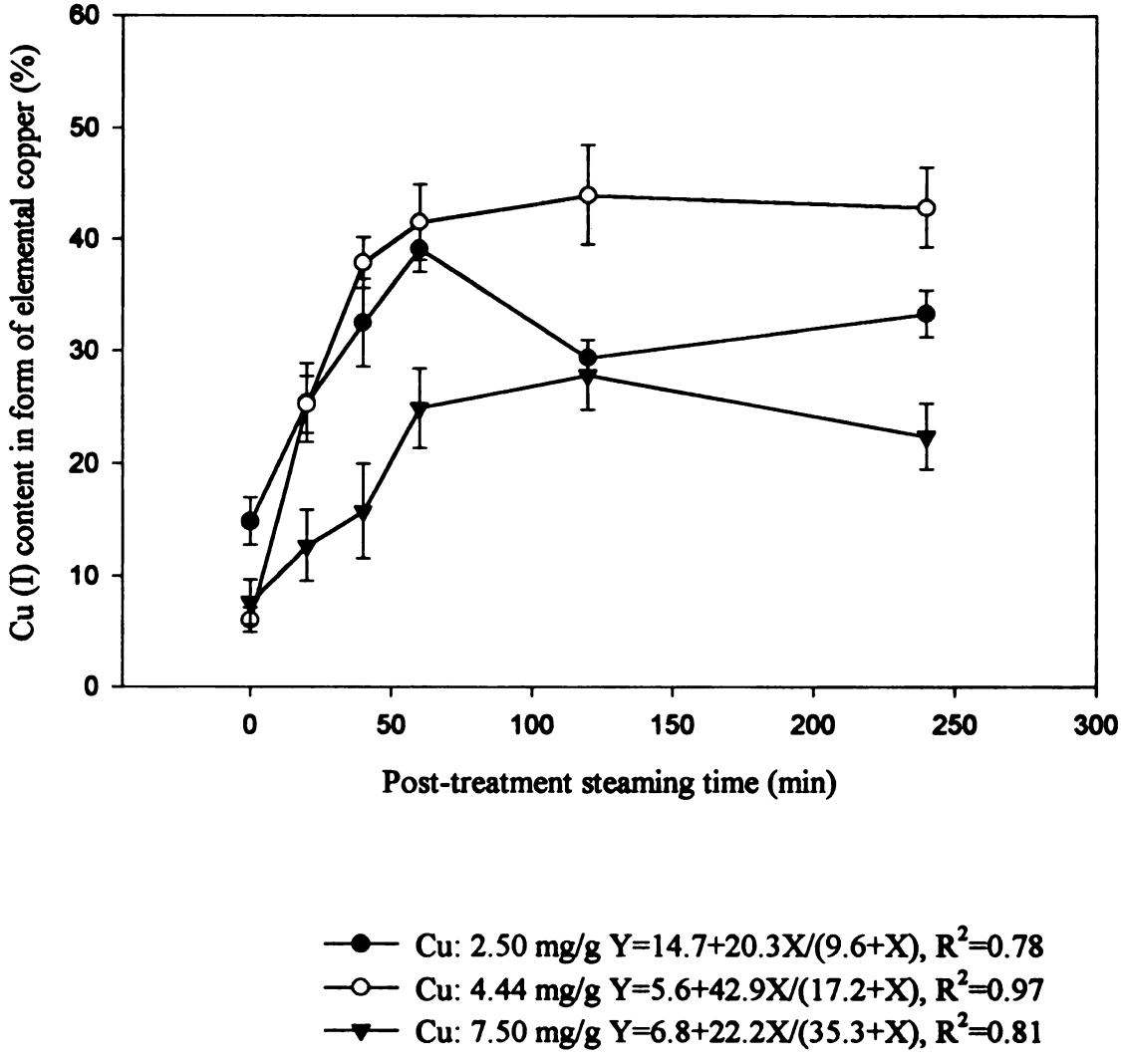


Figure 12. Cu (I) content in Cu-EA treated SM after post-treatment steaming

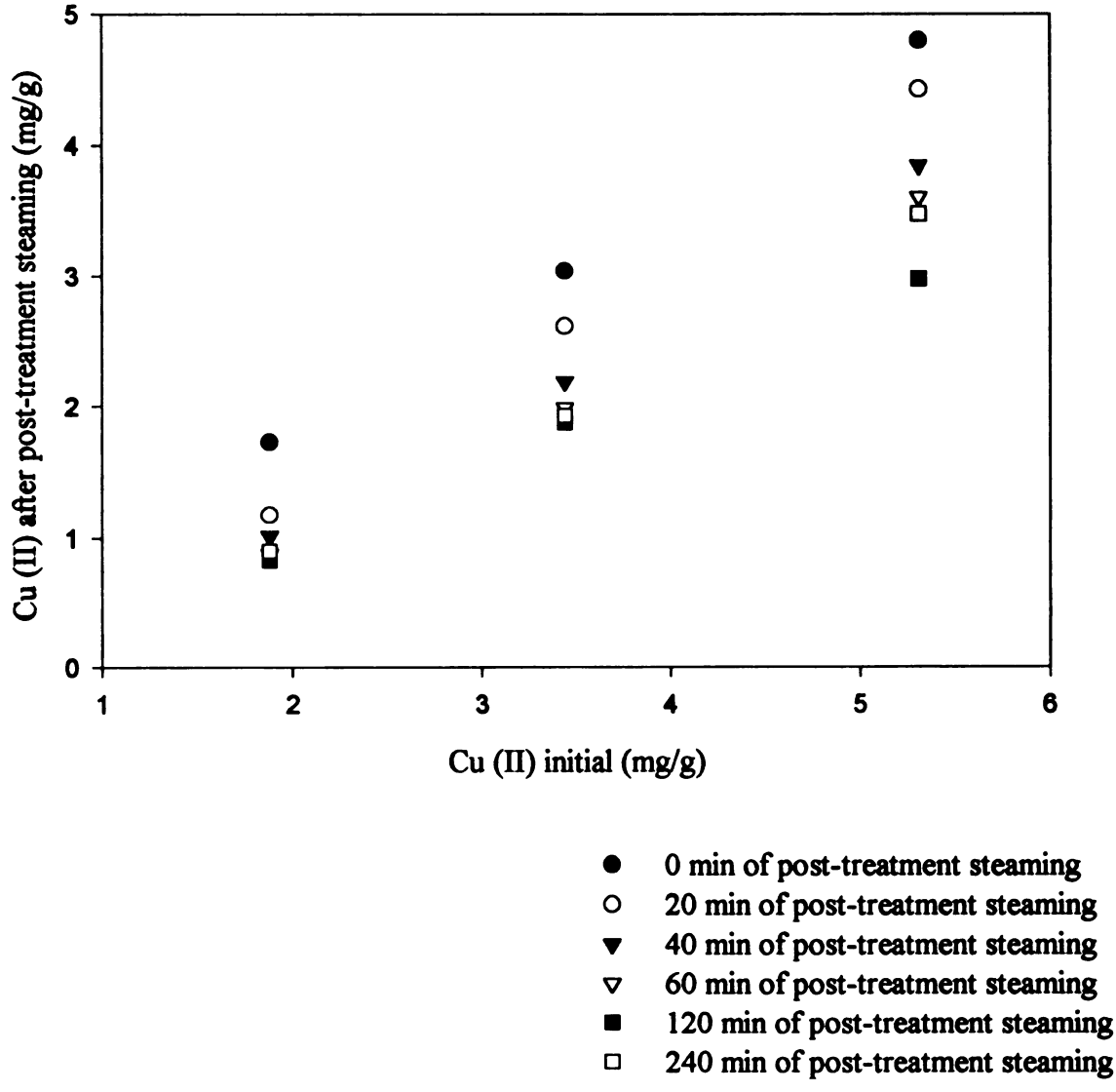


Figure 13. Cu (II) in Cu-N treated SYP after post-treatment steaming

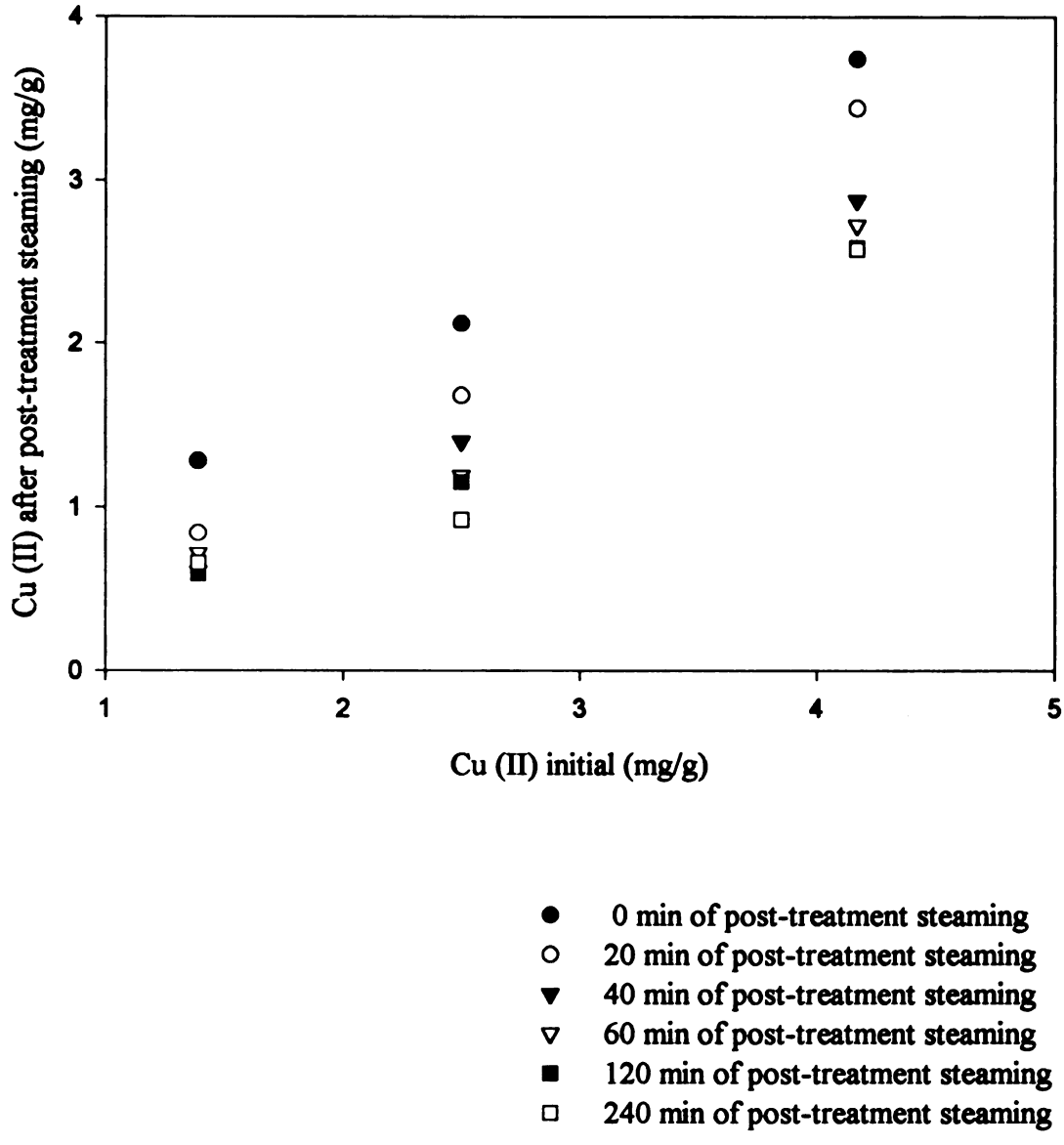


Figure 14. Cu (II) in Cu-N treated SM after post-treatment steaming

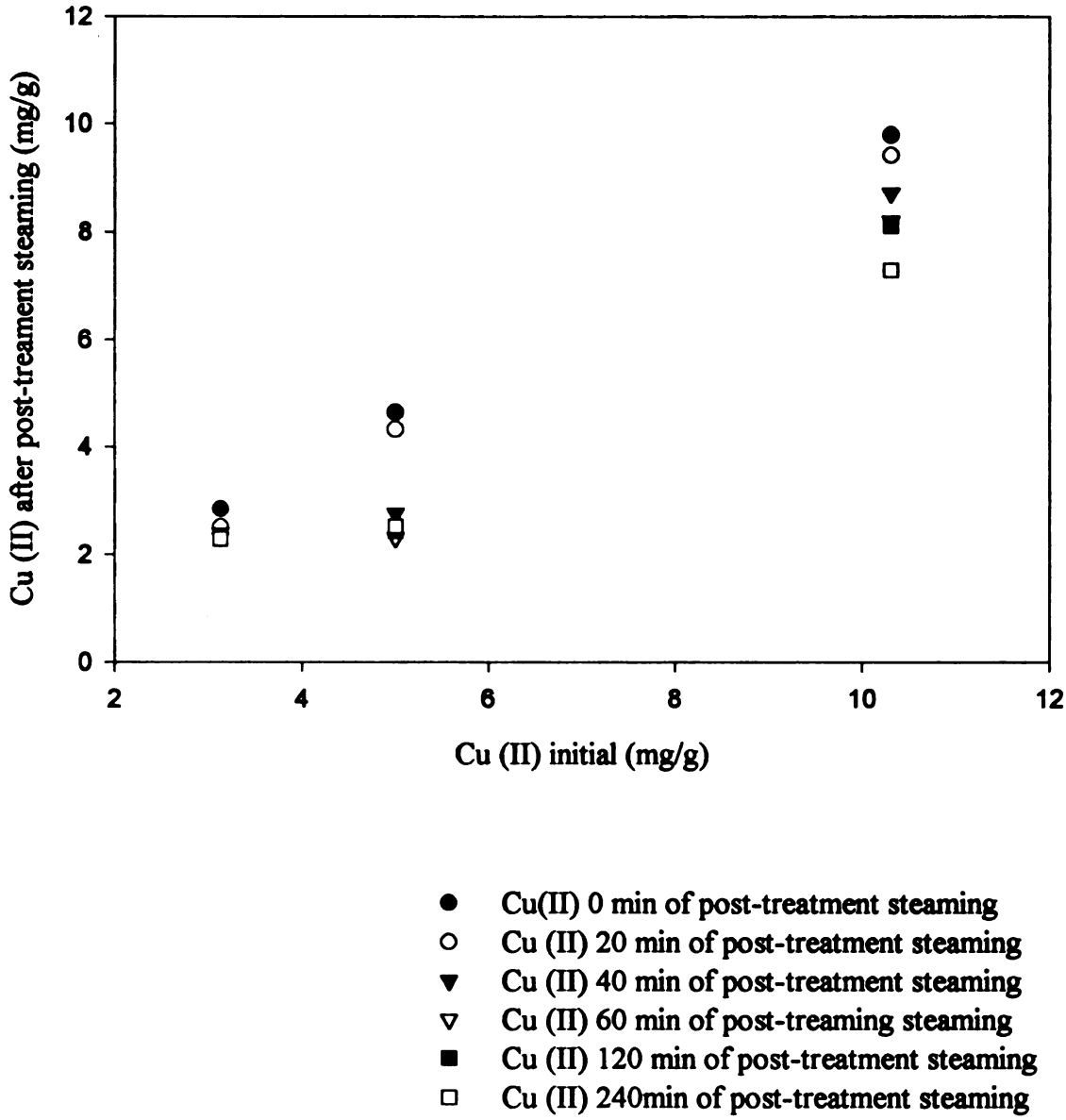


Figure 15. Cu (II) in Cu-EA treated SYP after post-treatment steaming

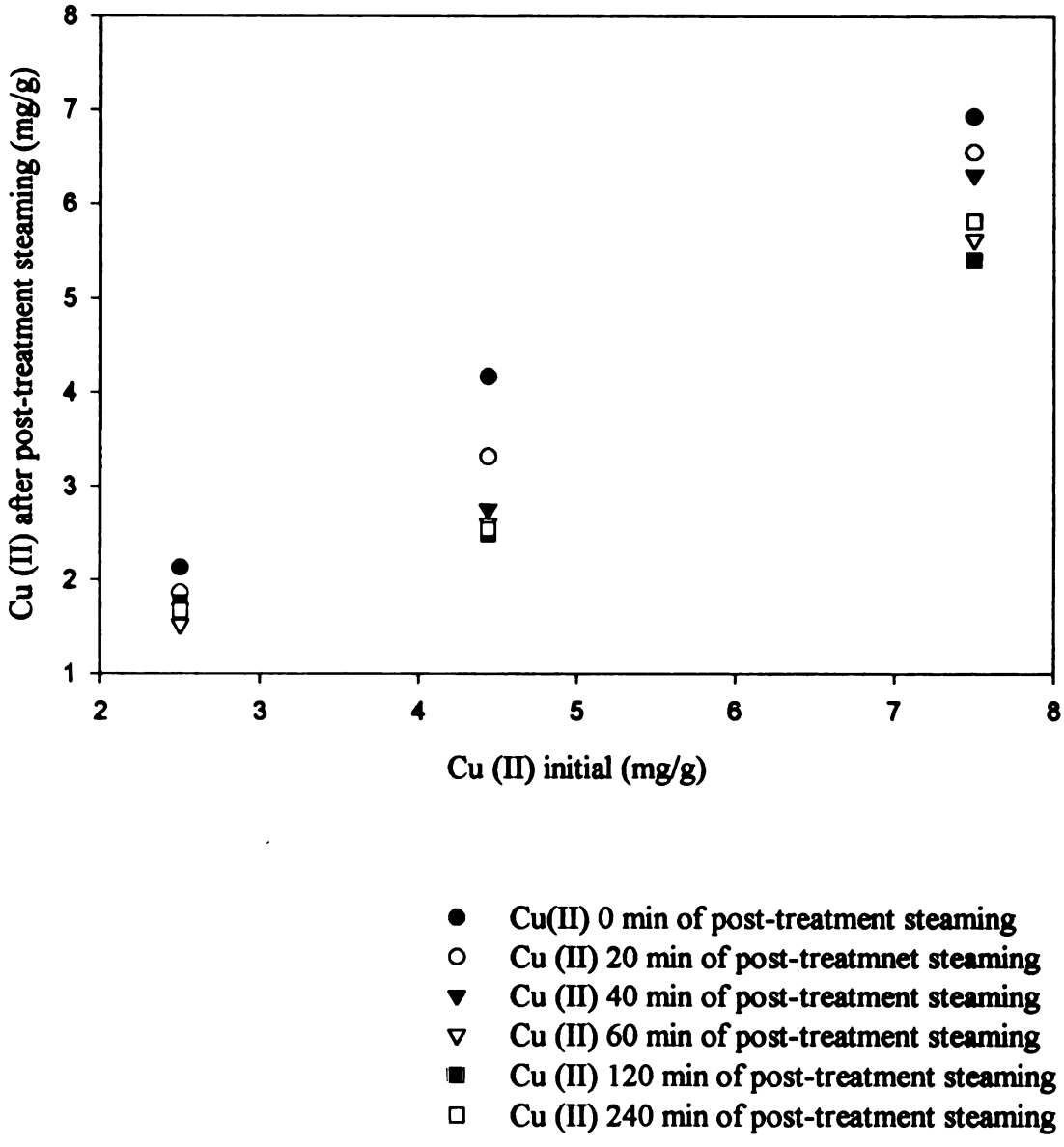


Figure 16. Cu (II) in Cu-EA treated SM after post-treatment steaming

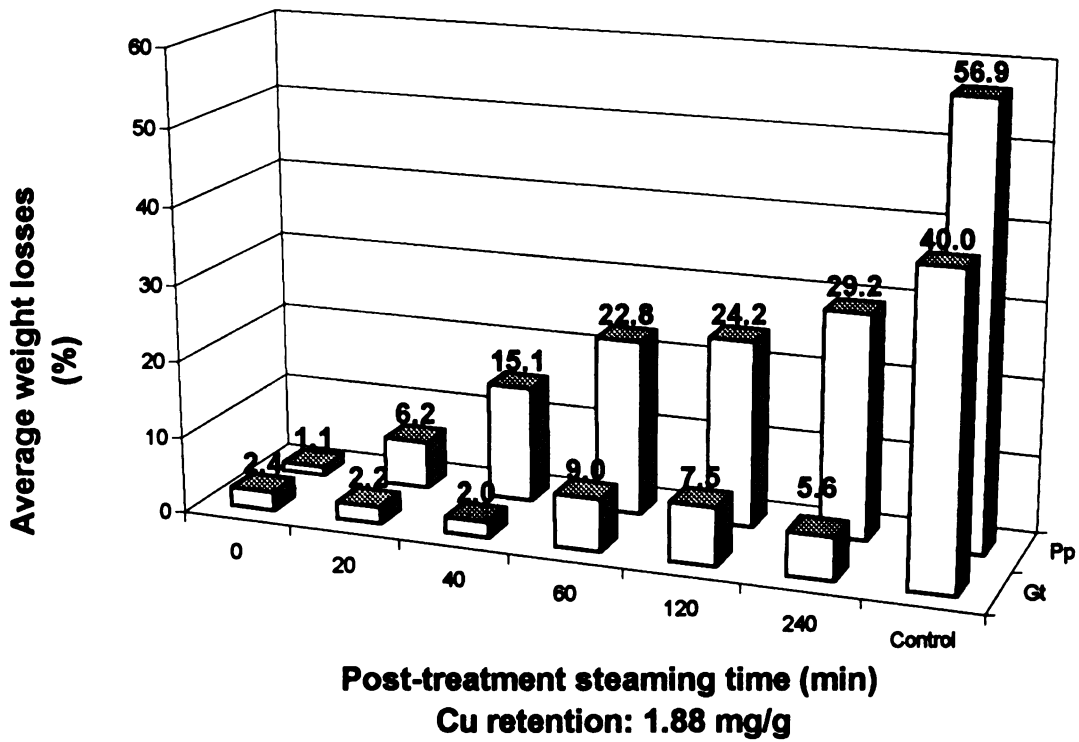


Figure 17. Average weight losses of Cu-N treated SYP to brown-rot fungi

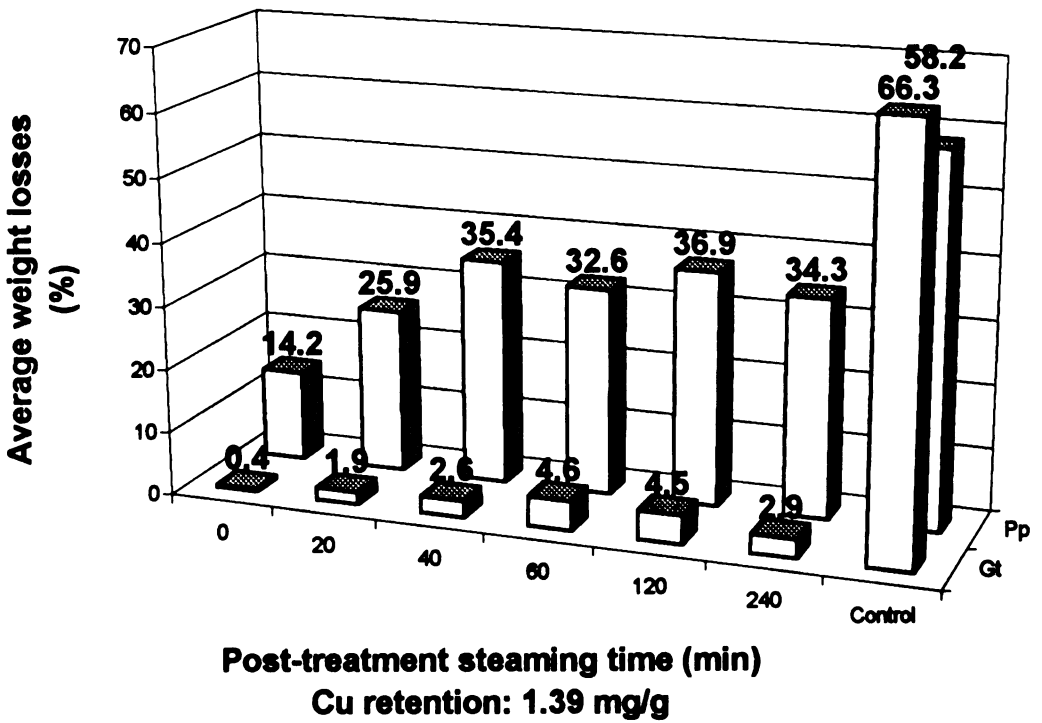


Figure 18. Average weight losses of Cu-N treated SM to brown-rot fungi

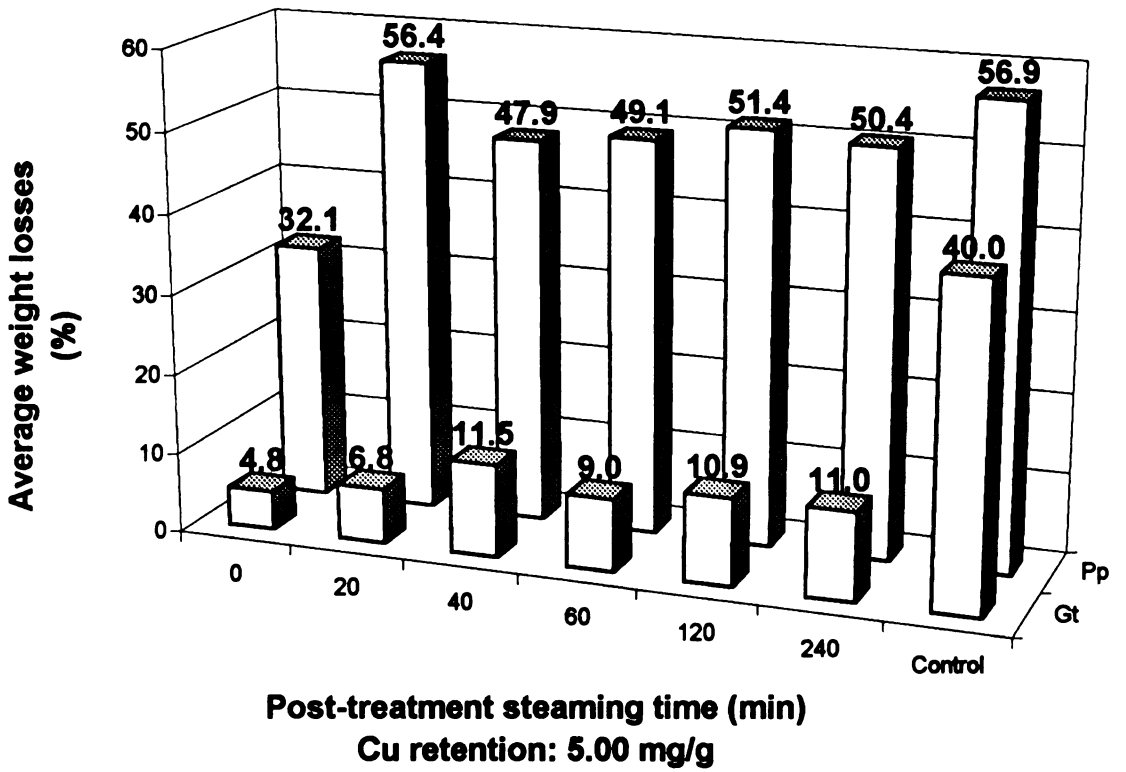


Figure 19. Average weight losses of Cu-EA treated SYP to brown-rot fungi

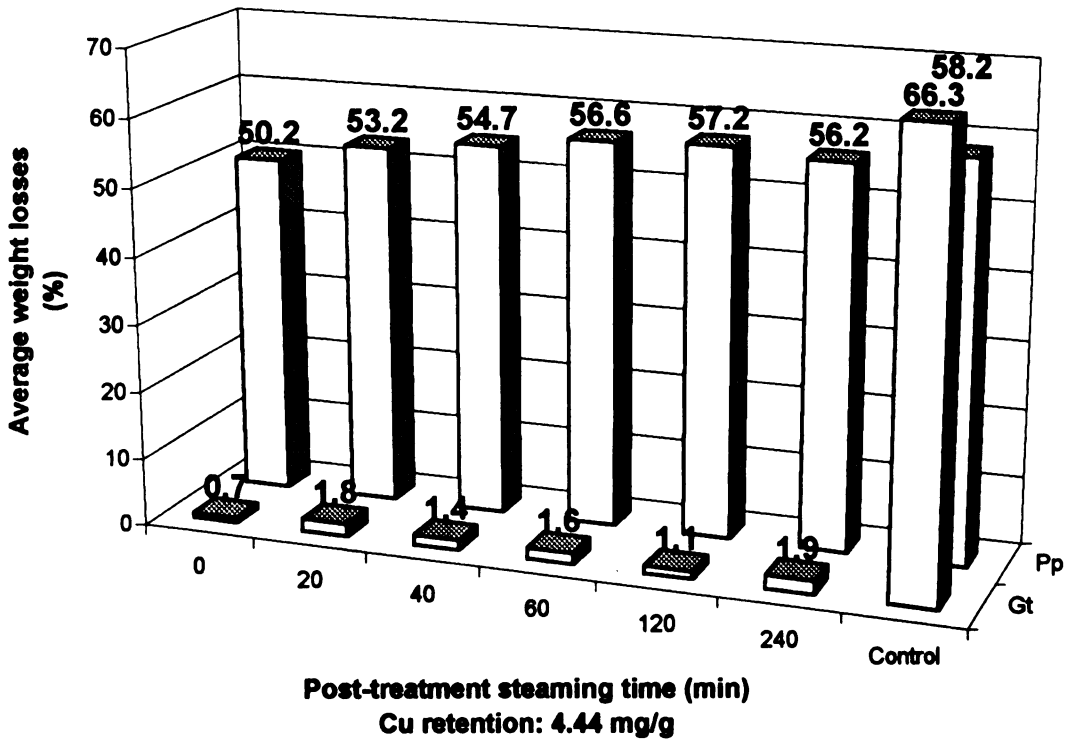


Figure 20. Average weight losses of Cu-EA treated SM to brown-rot fungi

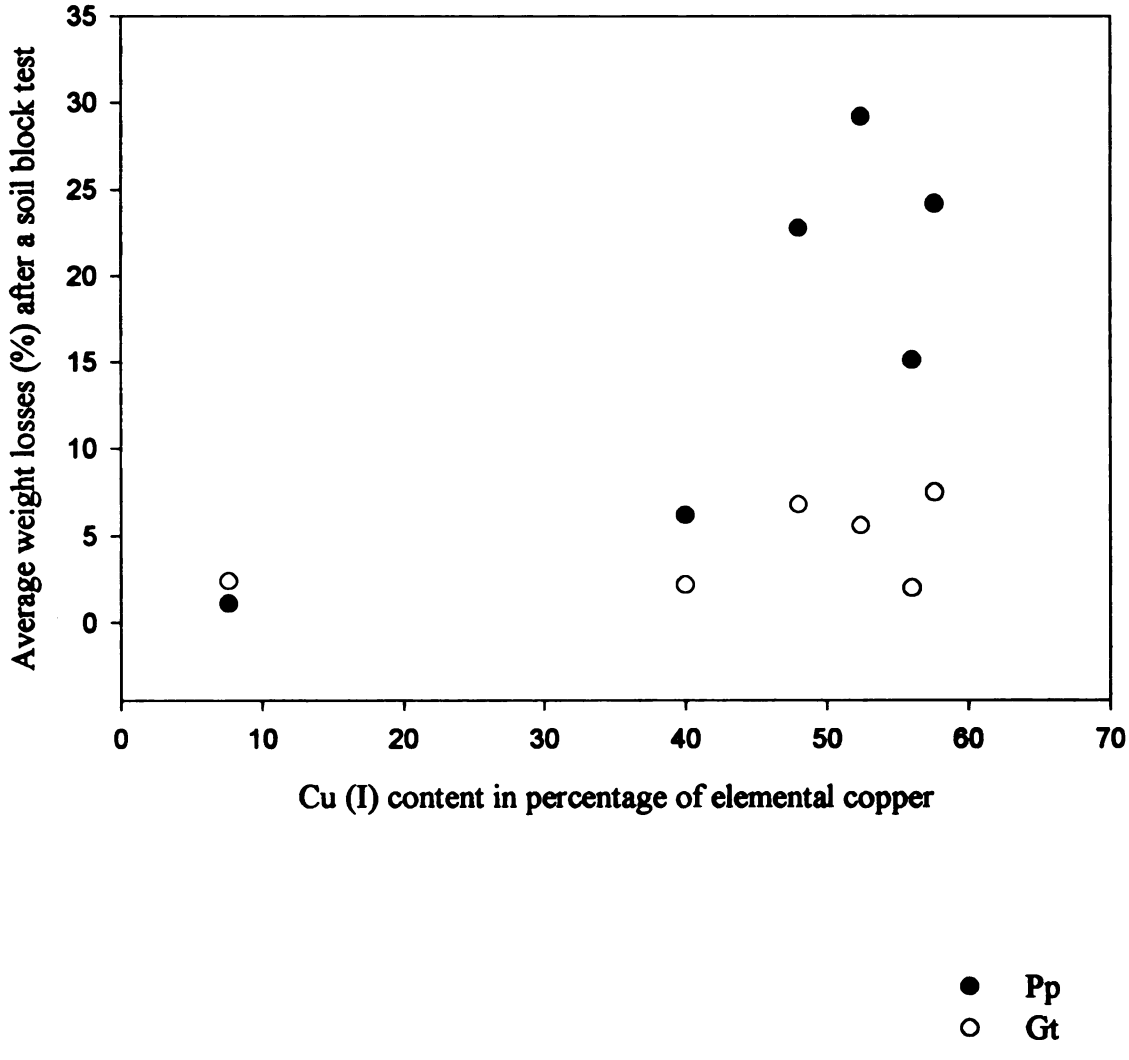


Figure 21. Average weight losses (%) after a soil block test versus the Cu (I) content (%) in Cu-N treated SYP (Cu retention: 1.88 mg/g)

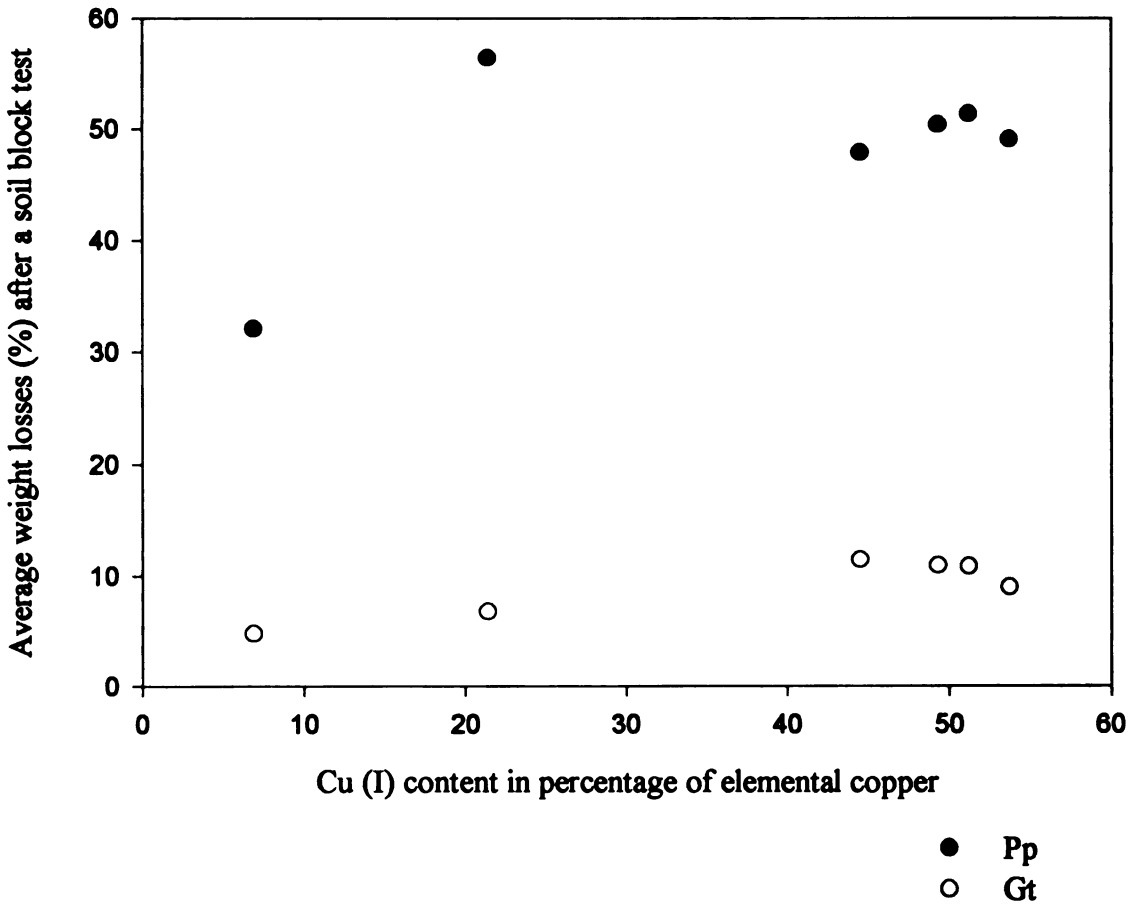


Figure 22. Average weight losses (%) after a soil block test versus the Cu (I) content (%) in Cu-EA treated SYP (Cu retention: 5.00 mg/g)

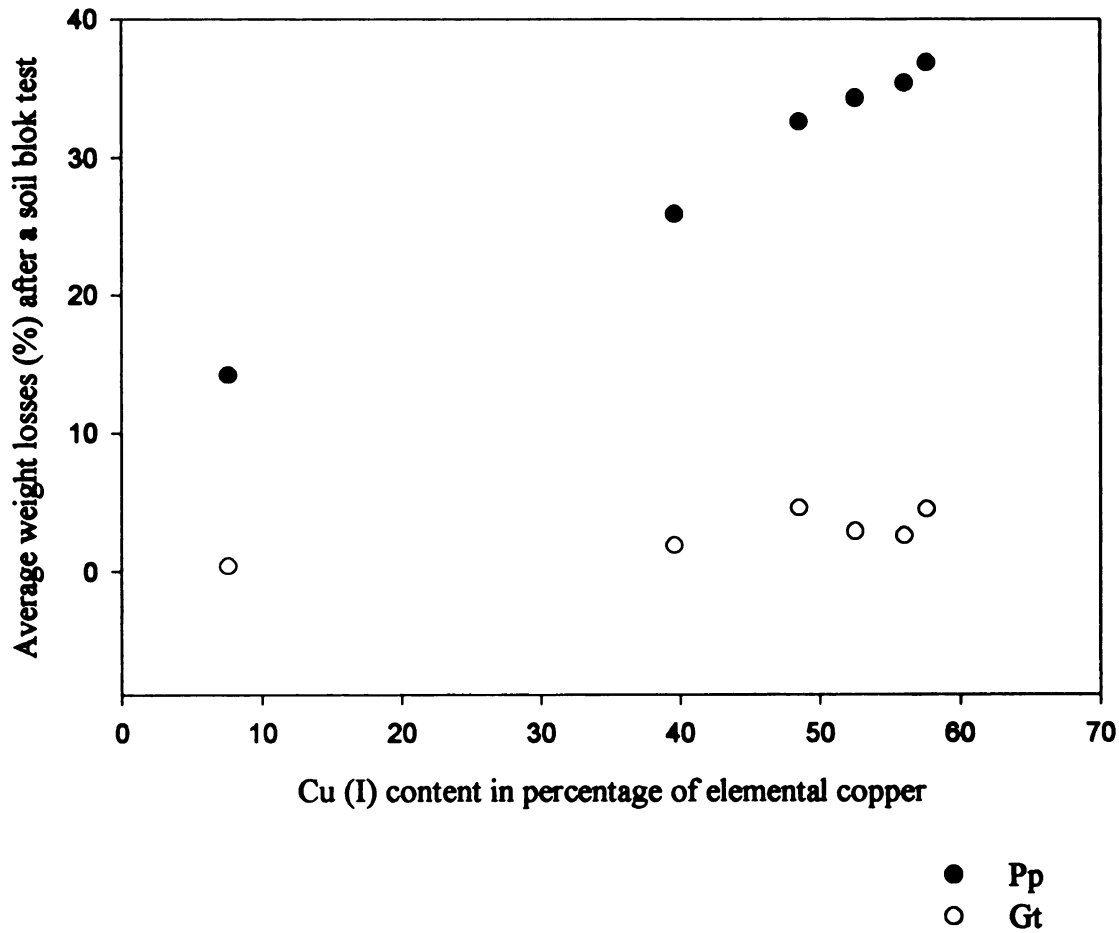


Figure 23. Average weight losses (%) after a soil block test versus the Cu (I) content (%) in Cu-N treated SM (Cu retention: 2.50 mg/g)

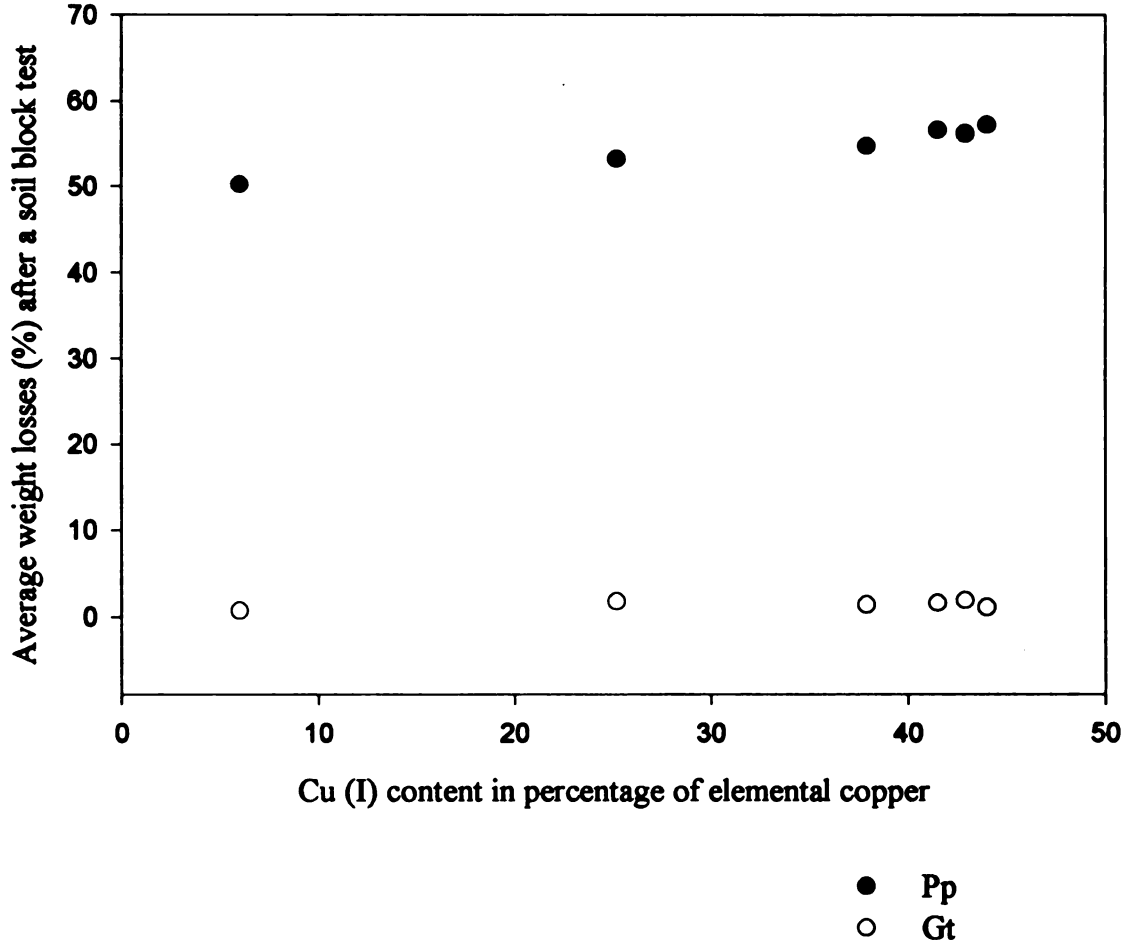


Figure 24. Average weight losses (%) after a soil block test versus the Cu (I) content (%) in Cu-EA treated SM (Cu retention: 4.44 mg/g)

APPENDIX

Initial data of weight of wood blocks for pressure treatment and soil block test

SYP	W_1(g)	W_2(g)	WG(g)	W_3(g)	W_4(g)	W_5(g)	WL(%)
Cu-EA Pp0min	1.05	2.67	1.62	1.16	1.68	0.73	37.1
Cu-EA Pp0min	1.07	2.83	1.76	1.18	0.79	0.44	62.7
Cu-EA Pp0min	1.13	2.86	1.73	1.21	1.71	0.80	33.9
Cu-EA Pp0min	1.14	2.87	1.73	1.24	1.89	0.80	35.5
Cu-EA Pp0min	1.05	2.72	1.67	1.20	2.41	0.95	20.8
Cu-EA Tv0min	1.06	2.72	1.66	1.12	1.68	1.04	7.1
Cu-EA Tv0min	1.07	2.76	1.69	1.13	1.54	1.04	8.0
Cu-EA Tv0min	1.11	2.70	1.59	1.20	1.46	1.09	9.2
Cu-EA Tv0min	1.04	2.47	1.43	1.10	1.41	1.02	7.3
Cu-EA Tv0min	1.11	2.89	1.78	1.20	1.84	1.09	9.2
Cu-EA Po0min	1.10	2.82	1.72	1.15	1.63	1.08	6.1
Cu-EA Po0min	1.15	2.70	1.55	1.17	1.91	1.13	3.4
Cu-EA Po0min	1.03	2.58	1.55	1.08	1.74	1.02	5.6
Cu-EA Po0min	1.06	2.62	1.56	1.09	1.75	1.04	4.6
Cu-EA Po0min	1.13	2.78	1.65	1.20	1.80	1.11	7.5
Cu-EA Gt0min	1.07	2.68	1.61	1.14	1.89	1.08	5.3
Cu-EA Gt0min	1.14	2.84	1.70	1.18	2.25	1.14	3.4
Cu-EA Gt0min	1.07	2.66	1.59	1.13	2.16	1.08	4.4
Cu-EA Gt0min	1.11	2.71	1.60	1.20	2.11	1.12	6.7
Cu-EA Gt0min	1.13	2.65	1.52	1.20	2.17	1.15	4.2
Cu-EA Pp20min	1.07	2.60	1.53	1.18	0.94	0.48	59.3
Cu-EA Pp20min	1.15	2.77	1.62	1.25	0.87	0.47	62.4
Cu-EA Pp20min	1.13	2.70	1.57	1.27	2.19	0.85	33.1
Cu-EA Pp20min	1.15	2.95	1.80	1.28	0.86	0.47	63.3
Cu-EA Pp20min	1.08	2.60	1.52	1.13	0.93	0.43	62.0
Cu-EA Tv20min	1.09	2.67	1.58	1.24	1.81	1.08	12.9
Cu-EA Tv20min	1.15	2.79	1.64	1.25	1.81	1.12	10.4

Cu-EA Tv20min	1.08	2.66	1.58	1.20	1.56	1.06	11.7
Cu-EA Tv20min	1.10	2.48	1.38	1.23	1.80	1.07	13.0
Cu-EA Tv20min	1.07	2.22	1.15	1.14	1.60	1.05	7.9
Cu-EA Gt20min	1.05	2.50	1.45	1.12	2.19	1.05	6.3
Cu-EA Gt20min	1.12	2.66	1.54	3.12	2.03	1.12	64.1
Cu-EA Gt20min	1.11	2.67	1.56	1.20	2.04	1.12	6.7
Cu-EA Gt20min	1.06	2.74	1.68	1.14	2.09	1.07	6.1
Cu-EA Gt20min	1.13	2.74	1.61	1.15	2.05	1.14	0.9
Cu-EA Po20min	1.08	2.74	1.66	1.12	1.90	1.06	5.4
Cu-EA Po20min	1.03	2.53	1.50	1.10	1.90	1.01	8.2
Cu-EA Po20min	1.15	2.74	1.59	1.17	1.96	1.12	4.3
Cu-EA Po20min	1.13	2.69	1.56	1.18	1.86	1.10	6.8
Cu-EA Po20min	1.14	2.71	1.57	1.16	2.04	1.11	4.3
Cu-EA Tv 40min	1.14	2.69	1.55	1.23	1.63	1.12	8.9
Cu-EA Tv 40min	1.13	2.61	1.48	1.24	1.79	1.10	11.3
Cu-EA Tv 40min	1.15	2.63	1.48	1.27	1.84	1.12	11.8
Cu-EA Tv 40min	1.14	2.79	1.65	1.26	1.66	1.12	11.1
Cu-EA Tv 40min	1.14	2.80	1.66	1.26	1.92	1.11	11.9
Cu-EA Pp40min	1.15	2.73	1.58	1.30	0.92	0.50	61.5
Cu-EA Pp40min	1.14	2.68	1.54	1.28	2.18	0.93	27.3
Cu-EA Pp40min	1.14	2.78	1.64	1.31	0.95	0.46	64.9
Cu-EA Pp40min	1.13	2.40	1.27	1.27	1.73	0.79	37.8
Cu-EA Pp40min	1.11	2.65	1.54	1.25	2.48	1.02	18.4
Cu-EA Gt40min	1.15	2.54	1.39	1.27	2.12	1.17	7.9
Cu-EA Gt40min	1.11	2.52	1.41	1.26	1.86	1.11	11.9
Cu-EA Gt40min	1.07	2.75	1.68	1.21	2.24	1.07	11.6
Cu-EA Gt40min	1.13	2.64	1.51	1.25	2.32	1.13	9.6
Cu-EA Gt40min	1.06	1.82	0.76	1.20	2.18	1.00	16.7
Cu-EA Po 40min	1.11	2.83	1.72	1.22	1.76	1.08	11.5
Cu-EA Po 40min	1.14	2.52	1.38	1.28	1.82	1.11	13.3
Cu-EA Po 40min	1.05	2.07	1.02	1.21	1.42	1.01	16.5

Cu-EA Po 40min	1.12	2.65	1.53	1.25	2.24	1.10	12.0
Cu-EA Po 40min	1.07	2.42	1.35	1.23	1.52	1.04	15.5
Cu-EA Pp60min	1.12	2.30	1.18	1.19	0.89	0.50	58.0
Cu-EA Pp60min	1.11	2.27	1.16	1.22	1.15	0.48	60.7
Cu-EA Pp60min	1.07	2.47	1.40	1.21	2.36	0.94	22.3
Cu-EA Pp60min	1.15	2.79	1.64	1.25	1.99	0.77	38.4
Cu-EA Pp60min	1.13	2.20	1.07	1.27	0.81	0.43	66.1
Cu-EA Gt60min	1.08	2.32	1.24	1.18	1.69	1.07	9.3
Cu-EA Gt60min	1.11	2.70	1.59	1.21	2.20	1.11	8.3
Cu-EA Gt60min	1.06	2.27	1.21	1.17	2.29	1.05	10.3
Cu-EA Gt60min	1.14	2.58	1.44	1.23	2.49	1.13	8.1
Cu-EA Gt60min	1.11	2.49	1.38	1.21	2.14	1.10	9.1
Cu-EA Tv60min	1.11	2.95	1.84	1.22	1.87	1.08	11.5
Cu-EA Tv60min	1.09	2.91	1.82	1.18	1.79	1.06	10.2
Cu-EA Tv60min	1.12	2.81	1.69	1.22	1.89	1.09	10.7
Cu-EA Tv60min	1.07	2.70	1.63	1.23	1.81	1.04	15.5
Cu-EA Tv60min	1.13	2.86	1.73	1.23	2.08	1.10	10.6
Cu-EA Po60min	1.09	2.79	1.70	1.21	2.00	1.06	12.4
Cu-EA Po60min	1.08	2.80	1.72	1.18	1.65	1.05	11.0
Cu-EA Po60min	1.06	2.66	1.60	1.17	1.84	1.04	11.1
Cu-EA Po60min	1.14	2.77	1.63	1.23	1.90	1.10	10.6
Cu-EA Po60min	1.11	2.82	1.71	1.21	1.87	1.08	10.7
Cu-E APp120min	1.04	2.72	1.68	1.18	1.19	0.57	51.7
Cu-EAPp120min	1.15	2.85	1.70	1.30	1.34	0.72	44.6
Cu-EA Pp120min	1.12	2.84	1.72	1.25	0.94	0.45	64.0
Cu-EA Pp120min	1.13	2.76	1.63	1.28	1.01	0.52	59.4
Cu-EA Pp120min	1.05	2.61	1.56	1.20	1.73	0.75	37.5
Cu-EA Gt120min	1.11	2.69	1.58	1.26	2.14	1.11	11.9
Cu-EA Gt120min	1.06	2.60	1.54	1.21	2.17	1.05	13.2
Cu-EA Gt120min	1.11	2.74	1.63	1.21	1.97	1.10	9.1
Cu-EA Gt120min	1.14	2.85	1.71	1.24	2.27	1.13	8.9

Cu-EA Gt120min	1.10	2.81	1.71	1.23	2.27	1.09	11.4
Cu-EA Tv120min	1.14	2.86	1.72	1.24	2.13	1.11	10.5
Cu-EA Tv120min	1.06	2.69	1.63	1.20	1.75	1.03	14.2
Cu-EA Tv120min	1.15	2.84	1.69	1.25	2.04	1.12	10.4
Cu-EA Tv120min	1.07	2.68	1.61	1.21	1.61	1.04	14.1
Cu-EA Tv120min	1.16	2.80	1.64	1.22	1.91	1.12	8.2
Cu-EA Po120min	1.14	2.81	1.67	1.25	1.73	1.10	12.0
Cu-EA Po120min	1.09	2.81	1.72	1.18	2.02	1.06	10.2
Cu-EA Po120min	1.12	2.76	1.64	1.23	2.10	1.08	12.2
Cu-EA Po120min	1.09	2.77	1.68	1.18	1.98	1.05	11.0
Cu-EA Po120min	1.08	2.65	1.57	1.19	1.85	1.06	10.9
Cu-EA Po240min	1.08	2.64	1.56	1.17	2.40	1.04	11.1
Cu-EA Po240min	1.15	2.77	1.62	1.28	1.98	1.10	14.1
Cu-EA Po240min	1.03	2.50	1.47	1.18	1.69	0.99	16.1
Cu-EA Po240min	1.13	2.83	1.70	1.27	1.66	1.08	15.0
Cu-EA Po240min	1.09	2.86	1.77	1.17	2.14	1.05	10.3
Cu-EA Tv240min	1.08	2.65	1.57	1.16	1.81	1.04	10.3
Cu-EA Tv240min	1.14	2.82	1.68	1.26	1.80	1.09	13.5
Cu-EA Tv240min	1.13	2.88	1.75	1.23	2.01	1.09	11.4
Cu-EA Tv240min	1.10	2.77	1.67	1.23	2.14	1.06	13.8
Cu-EA Tv240min	1.12	2.75	1.63	1.25	2.21	1.08	13.6
Cu-EA Gt240min	1.07	2.85	1.78	1.19	2.06	1.05	11.8
Cu-EA Gt240min	1.07	2.70	1.63	1.21	2.16	1.06	12.4
Cu-EA Gt240min	1.08	2.75	1.67	1.22	2.10	1.08	11.5
Cu-EA Gt240min	1.15	2.94	1.79	1.28	2.11	1.14	10.9
Cu-EA Gt240min	1.12	2.83	1.71	1.19	2.04	1.09	8.4
Cu-EA Pp240min	1.10	2.89	1.79	1.19	2.48	0.87	26.9
Cu-EA Pp240min	1.11	2.68	1.57	1.22	0.85	0.48	60.7
Cu-EA Pp240min	1.10	2.89	1.79	1.28	2.16	0.77	39.8
Cu-EA Pp240min	1.13	2.92	1.79	1.25	0.94	0.48	61.6
Cu-EA Pp240min	1.13	2.73	1.60	1.25	0.86	0.46	63.2

Cu-N Pp0min	1.03	2.12	1.09	1.17	2.38	1.17	0.0
Cu-N Pp0min	1.15	2.33	1.18	1.05	1.75	1.02	2.9
Cu-N Pp0min	1.10	2.32	1.22	1.25	2.05	1.24	0.8
Cu-N Pp0min	1.13	2.30	1.17	1.29	1.74	1.28	0.8
Cu-N Pp0min	1.05	2.26	1.21	1.20	1.80	1.19	0.8
Cu-N Tv0min	1.11	2.25	1.14	1.23	1.82	1.11	9.8
Cu-N Tv0min	1.10	2.21	1.11	1.21	1.88	1.15	5.0
Cu-N Tv0min	1.08	2.32	1.24	1.20	1.80	1.12	6.7
Cu-N Tv0min	1.10	2.08	0.98	1.19	1.91	1.15	3.4
Cu-N Tv0min	1.12	2.24	1.12	1.22	1.65	1.19	2.5
Cu-N Po0min	1.14	2.27	1.13	1.24	1.68	1.20	3.2
Cu-N Po0min	1.09	2.15	1.06	1.23	1.62	1.14	7.3
Cu-N Po0min	1.03	2.08	1.05	1.19	1.53	1.09	8.4
Cu-N Po0min	1.13	2.22	1.09	1.23	1.96	1.18	4.1
Cu-N Po0min	1.12	2.25	1.13	1.24	1.64	1.18	4.8
Cu-N Gt0min	1.13	2.18	1.05	1.25	2.47	1.23	1.6
Cu-N Gt0min	1.09	2.29	1.20	1.21	2.07	1.23	-1.7
Cu-N Gt0min	1.15	2.27	1.12	1.27	2.69	1.25	1.6
Cu-N Gt0min	1.05	2.14	1.09	1.23	2.52	1.18	4.1
Cu-N Gt0min	1.09	2.17	1.08	1.24	2.31	1.18	4.8
Cu-N Pp20min	1.05	2.19	1.14	1.22	1.72	1.18	3.3
Cu-N Pp20min	1.14	2.29	1.15	1.30	2.39	1.18	9.2
Cu-N Pp20min	1.11	2.20	1.09	1.32	1.80	1.24	6.1
Cu-N Pp20min	1.12	2.23	1.11	1.29	2.29	1.19	7.8
Cu-N Pp20min	1.13	2.23	1.10	1.31	2.26	1.25	4.6
Cu-N Tv20min	1.12	2.19	1.07	1.24	1.68	1.15	7.3
Cu-N Tv20min	1.13	2.27	1.14	1.23	2.30	1.17	4.9
Cu-N Tv20min	1.12	2.29	1.17	1.20	2.05	1.16	3.3
Cu-N Tv20min	1.15	2.26	1.11	1.27	1.92	1.18	7.1
Cu-N Tv20min	1.13	2.15	1.02	1.24	1.94	1.17	5.7
Cu-N Po20min	1.11	2.26	1.15	1.20	2.74	1.16	3.3

Cu-N Po20min	1.11	2.29	1.18	1.19	1.66	1.15	3.4
Cu-N Po20min	1.10	2.25	1.15	1.21	1.66	1.15	5.0
Cu-N Po20min	1.12	2.26	1.14	1.21	1.84	1.17	3.3
Cu-N Po20min	1.06	2.15	1.09	1.18	1.67	1.11	5.9
Cu-N Gt20min	1.12	2.19	1.07	1.20	2.13	1.22	-1.7
Cu-N Gt20min	1.14	2.22	1.08	1.23	2.61	1.19	3.3
Cu-N Gt20min	1.12	2.27	1.15	1.25	2.65	1.20	4.0
Cu-N Gt20min	1.13	2.27	1.14	1.23	2.42	1.21	1.6
Cu-N Gt20min	1.14	2.18	1.04	1.27	2.65	1.22	3.9
Cu-N Po40min	1.12	2.27	1.15	1.20	2.21	1.16	3.3
Cu-N Po40min	1.01	2.01	1.00	1.15	1.89	1.04	9.6
Cu-N Po40min	1.10	2.18	1.08	1.19	2.00	1.13	5.0
Cu-N Po40min	1.09	2.19	1.10	1.21	1.98	1.13	6.6
Cu-N Po40min	1.15	2.25	1.10	1.26	1.80	1.19	5.6
Cu-N Tv40min	1.07	2.04	0.97	1.19	1.51	1.09	8.4
Cu-N Tv40min	1.11	2.22	1.11	1.21	1.80	1.14	5.8
Cu-N Tv40min	1.03	2.15	1.12	1.15	1.42	1.06	7.8
Cu-N Tv40min	1.12	2.24	1.12	1.19	1.69	1.15	3.4
Cu-N Tv40min	1.08	2.13	1.05	1.20	1.66	1.13	5.8
Cu-N Gt40min	1.12	2.23	1.11	1.20	2.11	1.22	-1.7
Cu-N Gt40min	1.04	2.04	1.00	1.21	2.33	1.12	7.4
Cu-N Gt40min	1.08	2.17	1.09	1.22	1.98	1.18	3.3
Cu-N Gt40min	1.13	2.28	1.15	1.21	2.63	1.22	-0.8
Cu-N Gt40min	1.12	2.26	1.14	1.23	2.16	1.21	1.6
Cu-N Pp40min	0.99	1.94	0.95	1.29	2.23	1.09	15.5
Cu-N Pp40min	1.11	2.23	1.12	1.35	1.61	0.79	41.5
Cu-N Pp40min	1.13	2.34	1.21	1.32	2.59	1.11	15.9
Cu-N Pp40min	1.04	2.23	1.19	1.28	1.78	1.08	15.6
Cu-N Pp40min	1.13	2.27	1.14	1.35	2.56	1.17	13.3
Cu-N Po60min	1.10	2.17	1.07	1.30	1.65	1.14	12.3
Cu-N Po60min	1.06	2.15	1.09	1.23	1.66	1.12	8.9

Cu-N Po60min	1.14	2.24	1.10	1.27	1.83	1.19	6.3
Cu-N Po60min	1.13	2.20	1.07	1.25	1.61	1.17	6.4
Cu-N Po60min	1.09	2.23	1.14	1.27	1.69	1.15	9.5
Cu-N Tv60min	1.06	2.10	1.04	1.25	1.93	1.11	11.2
Cu-N Tv60min	1.15	2.27	1.12	1.31	2.01	1.19	9.2
Cu-N Tv60min	1.14	2.26	1.12	1.33	2.01	1.18	11.3
Cu-N Tv60min	1.06	2.12	1.06	1.25	1.76	1.11	11.2
Cu-N Tv60min	1.15	2.22	1.07	1.32	2.17	1.20	9.1
Cu-N Gt60min	1.13	2.27	1.14	1.30	2.27	1.22	6.2
Cu-N Gt60min	1.09	1.92	0.83	1.27	2.15	1.13	11.0
Cu-N Gt60min	1.15	2.22	1.07	1.28	2.63	1.22	4.7
Cu-N Gt60min	1.07	2.10	1.03	1.19	2.37	1.13	5.0
Cu-N Gt60min	1.15	2.23	1.08	1.32	2.63	1.23	6.8
Cu-N Pp60min	1.13	2.23	1.10	1.36	2.16	1.26	7.4
Cu-N Pp60min	0.99	1.97	0.98	1.33	2.18	1.03	22.6
Cu-N Pp60min	1.09	2.16	1.07	1.32	2.02	0.99	25.0
Cu-N Pp60min	1.11	2.27	1.16	1.39	2.38	1.11	20.1
Cu-N Pp60min	1.11	2.21	1.10	1.40	2.32	1.07	23.6
Cu-N Po120min	1.14	2.28	1.14	1.26	2.20	1.18	6.4
Cu-N Po120min	1.27	2.33	1.06	1.40	2.30	1.30	7.1
Cu-N Po120min	1.11	2.37	1.26	1.25	2.02	1.16	7.2
Cu-N Po120min	1.13	2.20	1.07	1.26	2.29	1.18	6.4
Cu-N Po120min	1.14	2.26	1.12	1.28	2.51	1.17	8.6
Cu-N Tv120min	1.15	2.26	1.11	1.30	2.07	1.19	8.5
Cu-N Tv120min	1.15	2.26	1.11	1.32	2.25	1.18	10.6
Cu-N Tv120min	1.07	2.30	1.23	1.27	1.96	1.11	12.6
Cu-N Tv120min	1.07	2.16	1.09	1.27	2.50	1.10	13.4
Cu-N Tv120min	1.11	2.17	1.06	1.30	1.94	1.13	13.1
Cu-N Gt120min	1.07	2.07	1.00	1.25	2.43	1.11	11.2
Cu-N Gt120min	1.11	2.25	1.14	1.31	2.70	1.22	6.9
Cu-N Gt120min	1.10	2.18	1.08	1.28	2.57	1.18	7.8

Cu-N Gt120min	1.15	2.23	1.08	1.32	2.05	1.23	6.8
Cu-N Gt120min	1.09	2.11	1.02	1.22	1.82	1.16	4.9
Cu-N Pp120min	1.13	2.31	1.18	1.28	1.17	0.96	25.0
Cu-N Pp120min	1.03	2.04	1.01	1.32	1.98	0.96	27.3
Cu-N Pp120min	1.12	2.43	1.31	1.35	2.52	1.15	14.8
Cu-N Pp120min	1.08	2.12	1.04	1.22	1.07	0.89	27.1
Cu-N Pp120min	1.15	2.24	1.09	1.20	1.77	0.88	26.7
Cu-N Pp240min	1.15	2.27	1.12	1.26	1.15	0.91	27.8
Cu-N Pp240min	1.15	2.29	1.14	1.24	1.22	0.84	32.3
Cu-N Pp240min	1.14	2.30	1.16	1.26	1.15	0.72	42.9
Cu-N Pp240min	1.06	2.10	1.04	1.24	2.19	1.02	17.7
Cu-N Pp240min	1.11	2.21	1.10	1.22	1.29	0.91	25.4
Cu-N Gt240min	1.12	2.29	1.17	1.22	2.58	1.20	1.6
Cu-N Gt240min	1.13	2.17	1.04	1.25	2.57	1.12	10.4
Cu-N Gt240min	1.13	2.25	1.12	1.24	2.58	1.16	6.5
Cu-N Gt240min	1.15	2.23	1.08	1.26	2.72	1.20	4.8
Cu-N Gt240min	1.13	2.25	1.12	1.25	2.54	1.19	4.8
Cu-N Tv240min	1.09	2.14	1.05	1.23	1.70	1.11	9.8
Cu-N Tv240min	1.15	2.23	1.08	1.28	2.13	1.16	9.4
Cu-N Tv240min	1.10	2.14	1.04	1.29	2.11	1.11	14.0
Cu-N Tv240min	1.05	2.16	1.11	1.23	2.00	1.07	13.0
Cu-N Tv240min	1.12	2.04	0.92	1.32	1.76	1.13	14.4
Cu-N Po240min	1.08	2.13	1.05	1.25	2.02	1.11	11.2
Cu-N Po240min	1.15	2.23	1.08	1.31	2.29	1.17	10.7
Cu-N Po240min	1.13	2.08	0.95	1.28	2.04	1.15	10.2
Cu-N Po240min	1.12	2.24	1.12	1.29	1.98	1.14	11.6
Cu-N Po240min	1.13	2.23	1.10	1.29	2.04	1.17	9.3
SM							
Cu-EAPp0min	2.68	5.48	2.80	2.71	1.83	1.30	52.0
Cu-EAPp0min	2.61	5.61	3.00	2.63	1.87	1.32	49.8
Cu-EAPp0min	2.47	5.16	2.69	2.48	1.75	1.26	49.2

Cu-EAPp0min	2.70	5.81	3.11	2.73	1.90	1.27	53.5
Cu-EAPp0min	2.66	5.73	3.07	2.70	2.10	1.49	44.8
Cu-EATv0min	2.65	5.71	3.06	2.69	4.98	2.52	6.3
Cu-EATv0min	2.54	5.45	2.91	2.57	4.53	2.38	7.4
Cu-EATv0min	2.52	5.42	2.90	2.55	4.25	2.31	9.4
Cu-EATv0min	2.60	5.45	2.85	2.64	4.86	2.37	10.2
Cu-EATv0min	2.45	5.39	2.94	2.48	3.62	2.29	7.7
Cu-EAGt0min	2.73	5.67	2.94	2.76	5.14	2.74	0.7
Cu-EAGt0min	2.65	5.76	3.11	2.68	5.06	2.66	0.8
Cu-EAGt0min	2.55	5.48	2.93	2.60	5.04	2.60	0.0
Cu-EAGt0min	2.59	5.47	2.88	2.62	5.05	2.62	0.0
Cu-EAGt0min	2.45	5.27	2.82	2.47	4.72	2.42	2.0
Cu-EAPo0min	2.51	5.54	3.03	2.56	4.58	2.36	7.8
Cu-EAPo0min	2.43	5.40	2.97	2.48	4.01	2.27	8.5
Cu-EAPo0min	2.66	5.29	2.63	2.71	4.69	2.36	12.9
Cu-EAPo0min	2.52	5.66	3.14	2.58	4.95	2.42	6.2
Cu-EAPo0min	2.83	6.12	3.29	2.85	4.25	2.60	8.8
Cu-EAPp20min	2.91	6.07	3.16	2.96	2.09	1.45	51.0
Cu-EAPp20min	2.33	5.13	2.80	2.40	1.77	1.26	47.5
Cu-EAPp20min	2.32	5.26	2.94	2.39	2.40	0.95	60.3
Cu-EAPp20min	2.61	5.55	2.94	2.68	1.92	1.35	49.6
Cu-EAPp20min	2.32	5.08	2.76	2.37	1.68	1.00	57.8
Cu-EATv20min	2.60	5.49	2.89	2.64	4.92	2.54	3.8
Cu-EATv20min	2.37	5.05	2.68	2.41	4.48	2.29	5.0
Cu-EATv20min	2.46	5.23	2.77	2.51	3.86	2.33	7.2
Cu-EATv20min	2.60	5.40	2.80	2.64	4.59	2.43	8.0
Cu-EATv20min	2.57	5.54	2.97	2.62	4.65	2.46	6.1
Cu-EAGt20min	2.55	5.29	2.74	2.60	4.90	2.54	2.3
Cu-EAGt20min	2.60	5.41	2.81	2.68	5.10	2.65	1.1
Cu-EAGt20min	2.51	5.18	2.67	2.60	4.79	2.57	1.2
Cu-EAGt20min	2.22	4.93	2.71	2.29	4.27	2.22	3.1

Cu-EAGt20min	2.52	5.49	2.97	2.59	5.09	2.55	1.5
Cu-EAPo20min	2.11	4.65	2.54	2.17	4.08	2.06	5.1
Cu-EAPo20min	2.43	5.47	3.04	2.51	4.65	2.38	5.2
Cu-EAPo20min	2.65	5.66	3.01	2.72	3.62	2.43	10.7
Cu-EAPo20min	2.60	5.63	3.03	2.64	4.47	2.52	4.6
Cu-EAPo20min	2.51	5.34	2.83	2.56	4.84	2.41	5.9
Cu-EAPo40min	2.50	5.19	2.69	2.54	4.80	2.42	4.7
Cu-EAPo40min	2.33	5.11	2.78	2.40	4.46	2.28	5.0
Cu-EAPo40min	2.37	5.27	2.90	2.42	4.13	2.32	4.1
Cu-EAPo40min	2.68	5.68	3.00	2.78	5.15	2.56	7.9
Cu-EAPo40min	2.52	5.43	2.91	2.62	4.54	2.50	4.6
Cu-EATv40min	2.43	5.32	2.89	2.51	3.82	2.40	4.4
Cu-EATv40min	2.50	5.57	3.07	2.58	4.57	2.47	4.3
Cu-EATv40min	2.49	5.28	2.79	2.55	4.72	2.36	7.5
Cu-EATv40min	2.60	5.60	3.00	2.67	4.15	2.49	6.7
Cu-EATv40min	2.60	5.70	3.10	2.68	5.07	2.56	4.5
Cu-EAGt40min	2.21	4.62	2.41	2.27	4.38	2.19	3.5
Cu-EAGt40min	2.61	5.38	2.77	2.66	4.95	2.61	1.9
Cu-EAGt40min	2.73	6.25	3.52	2.82	5.54	2.81	0.4
Cu-EAGt40min	2.44	5.33	2.89	2.54	5.26	2.52	0.8
Cu-EAGt40min	2.58	5.40	2.82	2.65	5.04	2.64	0.4
Cu-EAPp40min	2.67	5.48	2.81	2.74	2.01	1.37	50.0
Cu-EAPp40min	2.38	5.23	2.85	2.43	5.26	2.44	-0.4
Cu-EAPp40min	2.41	5.09	2.68	2.47	1.71	1.11	55.1
Cu-EAPp40min	2.40	4.33	1.93	2.46	1.65	1.09	55.7
Cu-EAPp40min	2.63	5.59	2.96	2.67	2.97	1.12	58.1
Cu-EAPp60min	2.40	5.22	2.82	2.44	3.61	1.00	59.0
Cu-EAPp60min	2.51	5.58	3.07	2.56	1.91	1.15	55.1
Cu-EAPp60min	2.48	5.43	2.95	2.56	2.29	1.17	54.3
Cu-EAPp60min	2.39	5.48	3.09	2.44	2.21	0.95	61.1
Cu-EAPp60min	2.31	5.16	2.85	2.40	1.69	1.12	53.3

Cu-EAGt60min	2.11	4.60	2.49	2.18	4.24	2.15	1.4
Cu-EAGt60min	2.32	5.16	2.84	2.40	4.47	2.37	1.3
Cu-EAGt60min	2.43	5.31	2.88	2.49	4.67	2.45	1.6
Cu-EAGt60min	2.40	5.45	3.05	2.48	4.84	2.43	2.0
Cu-EAGt60min	2.50	5.27	2.77	2.54	4.77	2.50	1.6
Cu-EATv60min	2.38	5.25	2.87	2.42	4.18	2.32	4.1
Cu-EATv60min	2.51	5.39	2.88	2.57	4.25	2.43	5.5
Cu-EATv60min	2.63	5.61	2.98	2.67	4.53	2.45	8.2
Cu-EATv60min	2.44	5.47	3.03	2.53	4.22	2.37	6.3
Cu-EATv60min	2.40	5.20	2.80	2.48	3.94	2.33	6.1
Cu-EAPo60min	1.99	4.46	2.47	2.06	4.01	1.99	3.4
Cu-EAPo60min	2.41	5.19	2.78	2.49	4.24	2.38	4.4
Cu-EAPo60min	2.18	4.48	2.30	2.23	3.38	2.04	8.5
Cu-EAPo60min	2.51	5.48	2.97	2.58	4.65	2.44	5.4
Cu-EAPo60min	2.42	5.38	2.96	2.49	4.57	2.35	5.6
Cu-EAPo120min	2.51	5.49	2.98	2.59	4.81	2.43	6.2
Cu-EAPo120min	2.52	5.28	2.76	2.60	4.84	2.43	6.5
Cu-EAPo120min	2.58	5.63	3.05	2.65	5.62	2.53	4.5
Cu-EAPo120min	2.60	5.19	2.59	2.66	3.89	2.33	12.4
Cu-EAPo120min	2.39	5.14	2.75	2.44	4.58	2.33	4.5
Cu-EATv120min	2.61	5.33	2.72	2.66	4.19	2.36	11.3
Cu-EATv120min	2.55	5.55	3.00	2.62	5.22	2.50	4.6
Cu-EATv120min	2.70	5.69	2.99	2.79	4.75	2.67	4.3
Cu-EATv120min	2.58	5.58	3.00	2.65	5.03	2.53	4.5
Cu-EATv120min	2.57	5.60	3.03	2.65	4.84	2.48	6.4
Cu-EAGt120min	2.43	5.45	3.02	2.55	5.15	2.52	1.2
Cu-EAGt120min	2.27	5.10	2.83	2.35	4.50	2.33	0.9
Cu-EAGt120min	2.30	5.11	2.81	2.38	4.61	2.37	0.4
Cu-EAGt120min	2.39	5.13	2.74	2.47	4.61	2.43	1.6
Cu-EAGt120min	2.48	5.46	2.98	2.56	4.99	2.52	1.6
Cu-EAPp120min	2.71	5.75	3.04	2.82	2.41	1.10	61.0

Cu-EAPp120min	2.24	5.00	2.76	2.38	1.66	1.01	57.6
Cu-EAPp120min	2.47	5.25	2.78	2.58	1.71	1.13	56.2
Cu-EAPp120min	2.38	5.16	2.78	2.46	1.76	1.23	50.0
Cu-EAPp120min	2.49	5.55	3.06	2.68	2.61	1.04	61.2
Cu-EAPo240min	2.38	5.16	2.78	2.42	4.90	2.30	5.0
Cu-EAPo240min	2.69	5.87	3.18	2.73	4.74	2.62	4.0
Cu-EAPo240min	2.39	5.23	2.84	2.44	4.07	2.29	6.2
Cu-EAPo240min	2.80	5.81	3.01	2.86	5.37	2.70	5.6
Cu-EAPo240min	2.46	5.29	2.83	2.51	4.72	2.34	6.8
Cu-EATv240min	2.60	5.62	3.02	2.65	3.94	2.44	7.9
Cu-EATv240min	2.55	5.28	2.73	2.61	3.98	2.43	6.9
Cu-EATv240min	2.51	5.41	2.90	2.58	4.62	2.45	5.0
Cu-EATv240min	2.51	5.49	2.98	2.58	5.04	2.47	4.3
Cu-EATv240min	2.41	4.96	2.55	2.47	4.59	2.34	5.3
Cu-EAGt240min	2.63	5.51	2.88	2.68	5.02	2.61	2.6
Cu-EAGt240min	2.02	4.43	2.41	2.08	4.40	2.05	1.4
Cu-EAGt240min	2.56	5.25	2.69	2.62	4.95	2.56	2.3
Cu-EAGt240min	2.55	5.43	2.88	2.63	4.91	2.61	0.8
Cu-EAGt240min	2.58	5.31	2.73	2.62	5.25	2.56	2.3
Cu-EAPp240min	2.53	5.37	2.84	2.61	1.73	1.11	57.5
Cu-EAPp240min	2.40	5.11	2.71	2.45	1.69	1.18	51.8
Cu-EAPp240min	2.50	5.20	2.70	2.56	1.92	1.01	60.6
Cu-EAPp240min	2.51	5.23	2.72	2.57	1.85	1.28	50.2
Cu-EAPp240min	2.50	5.39	2.89	2.57	4.06	1.00	61.1
Cu-N Pp0min	2.33	4.17	1.84	2.51	4.34	2.24	10.8
Cu-N Pp0min	2.31	4.33	2.02	2.54	3.95	2.61	-2.8
Cu-N Pp0min	2.12	4.00	1.88	2.37	4.16	2.06	13.1
Cu-N Pp0min	2.25	4.20	1.95	2.48	4.59	2.07	16.5
Cu-N Pp0min	2.37	4.10	1.73	2.58	4.53	2.16	16.3
Cu-N Tv0min	2.36	4.28	1.92	2.59	3.82	2.59	0.0
Cu-N Tv0min	2.38	4.22	1.84	2.61	4.71	2.60	0.4

Cu-N Tv0min	2.40	4.36	1.96	2.53	3.83	2.52	0.4
Cu-N Tv0min	2.32	4.23	1.91	2.51	4.17	2.52	-0.4
Cu-N Tv0min	2.31	4.33	2.02	2.49	4.50	2.47	0.8
Cu-N Po0min	2.21	4.15	1.94	2.40	4.47	2.41	-0.4
Cu-N Po0min	2.25	4.10	1.85	2.42	4.48	2.39	1.2
Cu-N Po0min	2.43	4.46	2.03	2.62	4.81	2.58	1.5
Cu-N Po0min	2.21	4.19	1.98	2.44	4.29	2.50	-2.5
Cu-N Po0min	2.25	4.31	2.06	2.49	4.74	2.50	-0.4
Cu-N Gt0min	2.60	4.52	1.92	2.72	4.85	2.73	-0.4
Cu-N Gt0min	2.47	4.24	1.77	2.60	4.73	2.58	0.8
Cu-N Gt0min	2.46	4.05	1.59	2.66	4.65	2.64	0.8
Cu-N Gt0min	2.72	4.34	1.62	2.89	4.86	2.86	1.0
Cu-N Gt0min	2.38	4.10	1.72	2.52	4.15	2.51	0.4
Cu-N Pp20min	2.43	4.42	1.99	2.58	2.79	1.92	25.6
Cu-N Pp20min	2.62	4.57	1.95	2.80	2.92	2.02	27.9
Cu-N Pp20min	2.58	4.39	1.81	2.73	4.67	1.94	28.9
Cu-N Pp20min	2.48	4.52	2.04	2.65	3.05	2.32	12.5
Cu-N Pp20min	2.66	4.74	2.08	2.84	5.03	2.24	21.1
Cu-N Tv20min	2.53	4.45	1.92	2.71	4.87	2.72	-0.4
Cu-N Tv20min	2.31	3.89	1.58	2.48	4.31	2.47	0.4
Cu-N Tv20min	2.50	4.38	1.88	2.62	4.61	2.60	0.8
Cu-N Tv20min	2.18	3.93	1.75	2.34	3.40	2.33	0.4
Cu-N Tv20min	2.28	4.17	1.89	2.49	3.74	2.49	0.0
Cu-N Gt20min	2.67	4.36	1.69	2.81	5.01	2.80	0.4
Cu-N Gt20min	2.58	4.45	1.87	2.75	4.45	2.68	2.6
Cu-N Gt20min	2.59	4.28	1.69	2.79	4.60	2.73	2.2
Cu-N Gt20min	2.41	4.16	1.75	2.59	4.61	2.51	3.1
Cu-N Gt20min	2.45	4.18	1.73	2.64	4.55	2.61	1.1
Cu-N Po20min	2.38	4.21	1.83	2.51	4.61	2.50	0.4
Cu-N Po20min	2.62	4.80	2.18	2.77	5.43	2.74	1.1
Cu-N Po20min	2.31	4.11	1.80	2.48	4.54	2.47	0.4

Cu-N Po20min	2.20	4.02	1.82	2.34	4.45	2.33	0.4
Cu-N Po20min	2.50	4.41	1.91	2.65	4.73	2.67	-0.8
Cu-N Po40min	2.31	4.44	2.13	2.57	5.05	2.56	0.4
Cu-N Po40min	2.32	4.16	1.84	2.51	4.91	2.50	0.4
Cu-N Po40min	2.33	4.24	1.91	2.55	4.45	2.56	-0.4
Cu-N Po40min	1.87	3.46	1.59	2.03	3.90	2.00	1.5
Cu-N Po40min	2.28	4.40	2.12	2.47	4.64	2.45	0.8
Cu-N Tv40min	2.37	4.30	1.93	2.52	4.14	2.51	0.4
Cu-N Tv40min	2.51	4.40	1.89	2.69	4.90	2.70	-0.4
Cu-N Tv40min	2.69	4.50	1.81	2.83	4.64	2.80	1.1
Cu-N Tv40min	2.40	4.34	1.94	2.57	4.71	2.58	-0.4
Cu-N Tv40min	2.43	4.36	1.93	2.60	4.03	2.58	0.8
Cu-N Gt40min	2.10	3.54	1.44	2.22	3.68	2.18	1.8
Cu-N Gt40min	2.59	4.42	1.83	2.78	4.32	2.73	1.8
Cu-N Gt40min	2.44	4.37	1.93	2.63	4.67	2.58	1.9
Cu-N Gt40min	2.56	4.41	1.85	2.74	4.56	2.66	2.9
Cu-N Gt40min	2.38	4.17	1.79	2.46	4.47	2.35	4.5
Cu-N Pp40min	2.32	4.25	1.93	2.49	4.15	1.70	31.7
Cu-N Pp40min	2.20	4.21	2.01	2.39	4.04	1.39	41.8
Cu-N Pp40min	2.25	4.09	1.84	2.40	4.98	2.53	-5.4
Cu-N Pp40min	2.28	4.03	1.75	2.50	3.12	1.39	44.4
Cu-N Pp40min	2.01	3.84	1.83	2.16	2.31	1.65	23.6
Cu-N Po60min	2.33	4.10	1.77	2.51	4.76	2.49	0.8
Cu-N Po60min	2.42	4.27	1.85	2.66	4.66	2.67	-0.4
Cu-N Po60min	2.41	4.34	1.93	2.56	4.80	2.52	1.6
Cu-N Po60min	2.58	4.33	1.75	2.70	4.88	2.68	0.7
Cu-N Po60min	2.31	4.10	1.79	2.48	4.74	2.48	0.0
Cu-N Tv60min	2.38	4.40	2.02	2.51	4.37	2.50	0.4
Cu-N Tv60min	2.49	4.41	1.92	2.64	5.05	2.63	0.4
Cu-N Tv60min	2.51	4.45	1.94	2.66	4.72	2.71	-1.9
Cu-N Tv60min	2.31	4.00	1.69	2.45	4.45	2.43	0.8

Cu-N Tv60min	2.42	4.32	1.90	2.59	4.76	2.58	0.4
Cu-N Gt60min	2.63	4.36	1.73	2.82	4.90	2.70	4.3
Cu-N Gt60min	2.48	4.54	2.06	2.64	4.60	2.59	1.9
Cu-N Gt60min	2.67	4.24	1.57	2.85	4.96	2.74	3.9
Cu-N Gt60min	2.56	4.20	1.64	2.65	3.88	2.47	6.8
Cu-N Gt60min	2.53	4.22	1.69	2.73	4.72	2.56	6.2
Cu-N Pp60min	2.58	4.59	2.01	2.79	2.78	2.05	26.5
Cu-N Pp60min	2.35	4.29	1.94	2.52	3.06	1.38	45.2
Cu-N Pp60min	2.49	4.39	1.90	2.68	5.05	2.95	-10.1
Cu-N Pp60min	2.31	4.05	1.74	2.43	4.19	1.66	31.7
Cu-N Pp60min	2.58	4.65	2.07	2.81	4.81	2.05	27.1
Cu-N Pp120min	2.32	4.22	1.90	2.56	4.47	1.56	39.1
Cu-N Pp120min	2.21	4.11	1.90	2.39	4.20	1.48	38.1
Cu-N Pp120min	2.27	3.95	1.68	2.45	2.41	1.60	34.7
Cu-N Pp120min	2.37	4.38	2.01	2.55	2.68	1.98	22.4
Cu-N Pp120min	2.20	4.02	1.82	2.40	3.86	1.19	50.4
Cu-N Gt120min	2.64	4.38	1.74	2.86	4.30	2.76	3.5
Cu-N Gt120min	2.72	4.45	1.73	2.92	4.82	2.74	6.2
Cu-N Gt120min	2.39	4.09	1.70	2.59	4.07	2.47	4.6
Cu-N Gt120min	2.44	4.08	1.64	2.64	4.23	2.49	5.7
Cu-N Gt120min	2.12	3.90	1.78	2.25	3.84	2.19	2.7
Cu-N Tv120min	2.18	4.16	1.98	2.38	4.59	2.39	-0.4
Cu-N Tv120min	2.70	4.70	2.00	2.99	5.29	2.97	0.7
Cu-N Tv120min	2.35	4.10	1.75	2.50	3.81	2.50	0.0
Cu-N Tv120min	2.31	4.22	1.91	2.46	4.28	2.45	0.4
Cu-N Tv120min	2.33	4.21	1.88	2.45	4.11	2.42	1.2
Cu-N Po120min	2.40	4.33	1.93	2.57	5.07	2.56	0.4
Cu-N Po120min	2.32	4.10	1.78	2.44	4.59	2.42	0.8
Cu-N Po120min	2.41	4.24	1.83	2.58	5.03	2.57	0.4
Cu-N Po120min	2.37	4.26	1.89	2.46	4.70	2.44	0.8
Cu-N Po120min	2.43	4.30	1.87	2.60	4.35	2.64	-1.5

Cu-N Pp240min	2.21	3.96	1.75	2.35	3.99	1.62	31.1
Cu-N Pp240min	2.31	4.22	1.91	2.46	4.09	1.38	43.9
Cu-N Pp240min	2.38	3.96	1.58	2.50	2.43	1.75	30.0
Cu-N Pp240min	2.41	4.36	1.95	2.57	2.50	1.57	38.9
Cu-N Pp240min	2.23	4.04	1.81	2.39	2.39	1.73	27.6
Cu-N Tv240min	2.42	4.20	1.78	2.55	4.79	2.54	0.4
Cu-N Tv240min	2.41	4.27	1.86	2.62	4.97	2.60	0.8
Cu-N Tv240min	2.23	4.16	1.93	2.34	4.45	2.31	1.3
Cu-N Tv240min	2.10	3.79	1.69	2.23	4.19	2.27	-1.8
Cu-N Tv240min	2.41	4.28	1.87	2.56	4.13	2.53	1.2
Cu-N Po240min	2.47	4.26	1.79	2.62	5.00	2.60	0.8
Cu-N Po240min	2.40	4.04	1.64	2.58	4.52	2.59	-0.4
Cu-N Po240min	2.63	4.40	1.77	2.80	4.83	2.77	1.1
Cu-N Po240min	2.00	3.59	1.59	2.08	4.34	2.07	0.5
Cu-N Po240min	2.23	4.04	1.81	2.40	4.53	2.42	-0.8
Cu-N Gt240min	2.19	3.80	1.61	2.37	4.26	2.31	2.5
Cu-N Gt240min	2.78	4.47	1.69	2.95	5.00	2.89	2.0
Cu-N Gt240min	2.40	4.21	1.81	2.51	4.46	2.40	4.4
Cu-N Gt240min	2.63	4.34	1.71	2.63	4.58	2.72	-3.4
Cu-N Gt240min	2.73	4.37	1.64	2.73	5.06	2.79	-2.2

W_1: weight of wood block after dried in oven at 40°C
W_2: initial weight of wood block after pressure treatment
W_3: weight of wood block dried in an oven at 40°C after pressure treatment
W_4: initial weight of wood block after a soil block test
W_5: weight of wood block dried in an oven at 40°C after a soil block test
WG: difference in weight of wood blocks before and after pressure treatment
WL: difference in weight of wood blocks before and after a soil block test in form of the weight of wood blocks before a soil block test
Treating solutions: 0.25% Cu-N and 0.5% Cu-EA (w/w in elemental copper)

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