Potentials of Nanotechnology Application in Forest Protection

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Abstract
This joint research project formed by Southern University, Louisiana State University and the USDA Forest Service focuses on applying nanotechnology in forest health and natural resource management. The targeted nanotechnology is derived from a new generation of renewable composite nano-material called Copper-Carbon Core-Shell Nanoparticles (CCCSNs), which have received increasing attention because of their low cost, unique stabilities, and demonstrated performance against Formosan termite and fungal diseases. This paper describes (1) the physical and chemical properties of CCCSNs and their interactions with environment, (2) CCCSNs uptake/distribution patterns within tree seedlings/mature trees and their effects on tree growth, and (3) the effects of CCCSNs on blue-stain and white rot fungi, and Formosa termite control. The goal of our research is to develop safe and effective formulations and treatment strategies, which use nanotechnology to protect forest and forest products against decay fungi and termites.

Introduction
The development of science and technology at the nanoscale revolutionizes our ability to manipulate and fabricate the engineered nanomaterials and nanosized subjects. Nanomaterials have generated tremendous interests because they offer many opportunities to deliver unprecedented material performance. Metal-based nanoparticles such as Cu, Au, Ag, etc., have been used as industrial chemicals, catalysts, optical media, electrode and magnetic materials. However, because of their high surface area-to-volume ratio, many metallic nanoparticles often have a high propensity to readily oxidize or otherwise undergo other chemical reactions. To minimize this problem a protective layer may be formed around the metal nanoparticles. Metal-carbon core-shell nanoparticles, which have a metallic core encased by a carbon shell, can extend the life and broaden the uses of metallic nanoparticles. The metal cores in such nanoparticles are protected against chemical reactions, and the carbon shells may be functionalized to have specific physical, chemical, and biological properties. There exists an unfilled need for metallic nanoparticles that are stable in air and water, yet still exhibit desirable chemical properties, as well as a method of generating such metallic nanoparticles that is cost efficient and scalable for industrial use. This paper introduces a new generation of renewable composite nano-material called Copper-Carbon Core-Shell Nanoparticles (CCCSNs), which have a copper core encased by a carbon shell. Because of their low cost, unique stability, and demonstrated performance against Formosan termite and fungal diseases, the CCCSNs have great potentials in applications for forest protection. In this paper, we describe (1) the basic physical and chemical properties of CCCSNs and their interactions with environment, (2) the CCCSNs uptake/distribution patterns in tree seedlings and their effects on tree growth, and (3) the effects of CCCSNs on blue-stain and white rot fungi, and Formosa termite control. This is part of a joint research project formed by Southern University, Louisiana State University and USDA Forest Service that focuses on applying nanotechnology in forest health and natural resource management. The goal of our research is to develop safe and effective formulations and treatment strategies that use nanotechnology to protect forest and forest products against decay fungi and termites, thus, helping secure our natural resources and economy.

Characterization of Copper-Carbon Core-Shell Nanoparticles (CCCSNs)
The CCCSNs are produced under a technology patent (US Patent Pending 60/772.325) using cotton fiber as a template. The fabricated products contain CCCSNs in carbon black and yellow powder (Figure 1). The CCCSNs can be suspended in water and oil (Figure 1). Analysis by TEM shows that CCCSNs are embedded in the porous carbon black substrate (Figure 2, left) and the cooper core and carbon shell structure is formed during one step fabricating process (Figure 2, left, inset). The size of CCCSNs averages 50 nm with a range of 20-60nm. The carbon shell averages 5nm with a range of 2-10nm. The CCCSNs possess a unique stability when immersed in water or exposed to air. For instance, after 36 months of immersion in water under the ambient atmosphere, the CCCSNs are able to maintain their original structure (Figure 2, right). X-ray diffraction shows little to no change in the nanoparticle's copper core after the immersion exposure and the carbon shell protects the copper core, which

remains as Cu zero (Figure 2, right, inset). Our research also shows that the CCCSNs possess good chemical stability in various pH solutions. The analysis of conductivity of CCCSNs in different pH solutions (pH4-pH9) over a two-month period indicates no significant copper ion leaching out of CCCSNs (Figure 3).

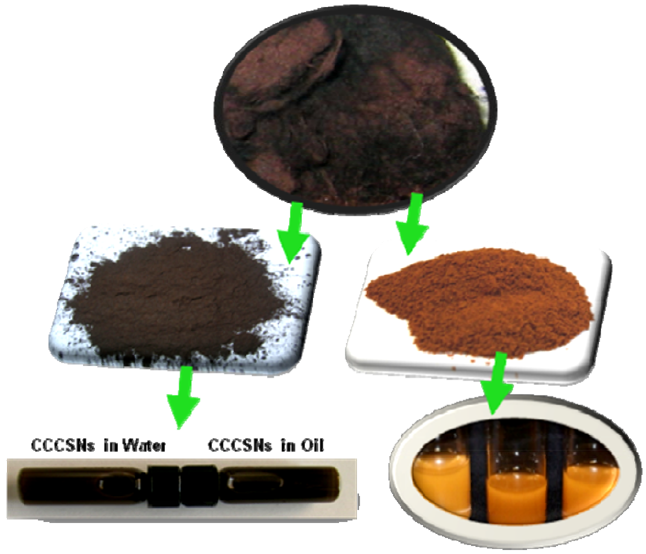


Figure 1. CCCSNs shown here are produced using cotton fiber and copper sulfate solution through one step processing. The fabricated products contain CCCSNs distributed in carbon black from cellulosic material (left) and yellow powder (right). The CCCSNs can be suspended in water and oil.

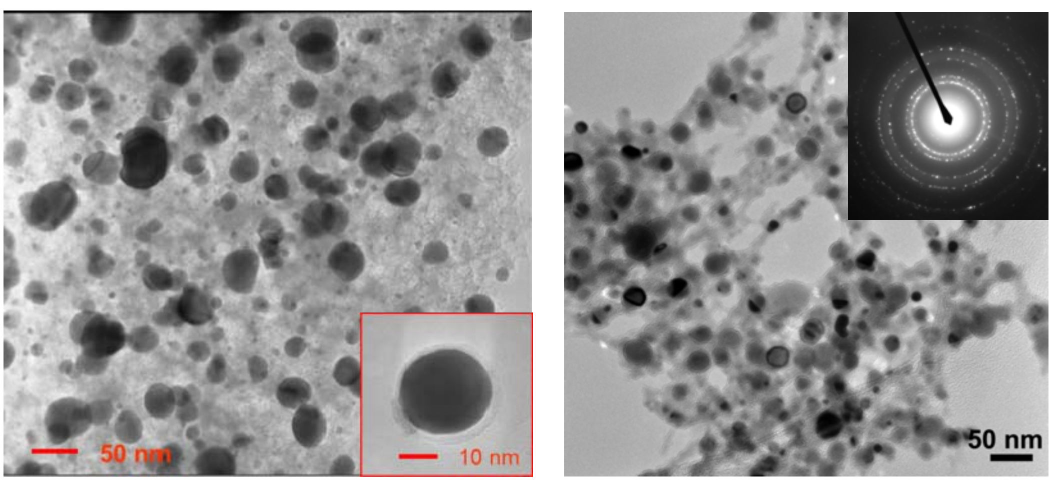


Figure 2. Left: TEM micrograph shows that CCCSNs are embedded in the porous carbon black substrate. The core shell structure (inset) is formed during one step fabricating process. Right: TEM image shows the stability of CCCSNs after 36 months of immersion in water under ambient atmosphere. X-ray diffraction (inset) shows no change to the nanoparticle's copper core after the exposure.

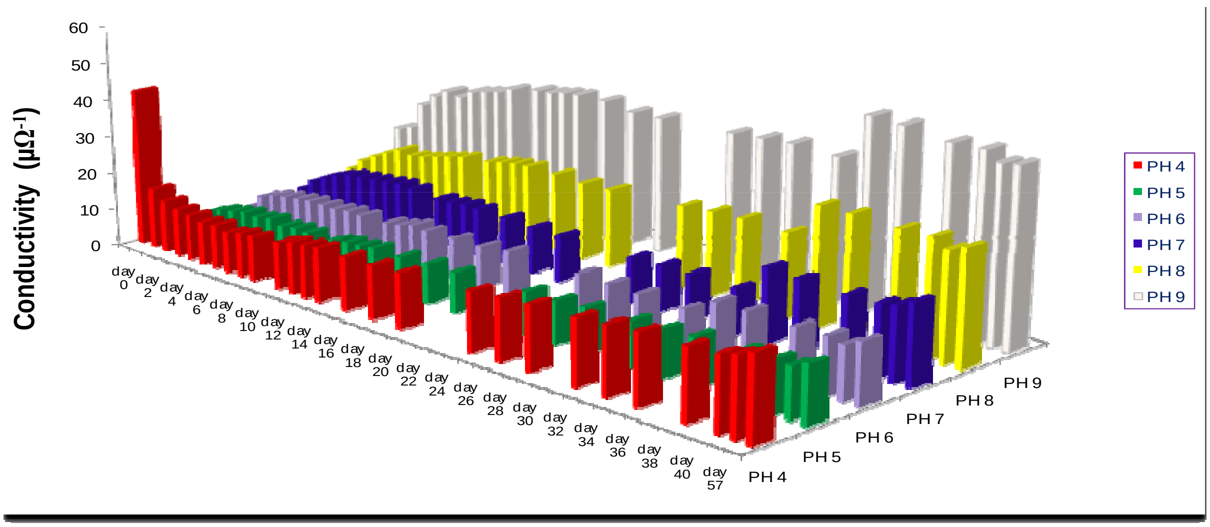


Figure 3. CCCSNs possess good chemical stability. The above chart shows the conductivity as a function of immersion time of carbon black powder containing CCCSNs in different pH solutions, indicating no significant copper ion leaching out of CCCSNs.

CCCSNs Uptake/Distribution Patterns in Tree Seedlings and Their Effects on Tree Growth
Understanding the effects of CCCSNs on tree physiology is the first step toward any future application in forestry. In this case, we used bald cypress (*Taxodium distichum*) for a preliminary test. Bald cypress is a wetland species that is an ideal study subject for testing CCCSNs effects on tree physiology in water saturated environment. Our study indicates that CCCSNs can enhance Cu uptake in bald cypress seedlings but show no significant effects on height, diameter, and biomass growth of the seedlings (Figures 4 and 5).

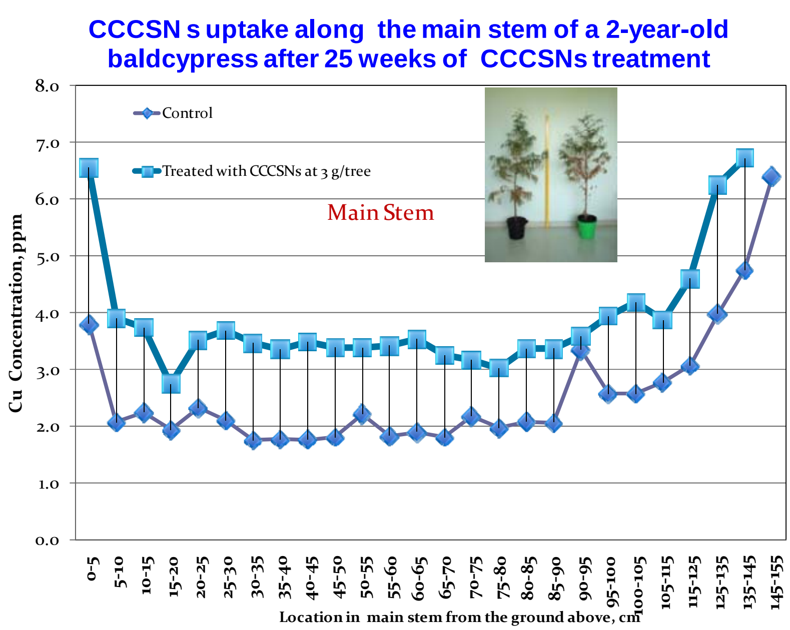


Figure 4. CCCSNs enhance Cu uptake along the main stem of a 2-yr-old bald cypress seedling after 25 weeks of CCCSNs treatment. The inset photo shows the bald cypress control (left) and CCCSNs treated (right) seedlings.

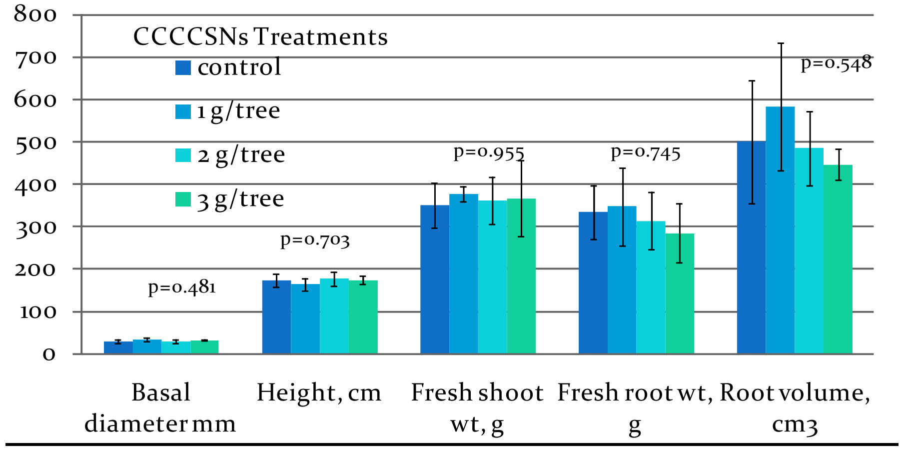


Figure 5. CCCSNs treatments show no significant effects on diameter, height, shoot and root weight, and root volume of bald cypress seedlings after 20 months of the treatments.

Effects of CCCSNs on Blue Stain and White Rot Fungi, and Formosa Termite Control
Our studies have shown that wood treated with CCCSNs is highly resistant to a common white rot decay fungus (*Trametes versicolor)* (Figure 6). White rot fungi are a major group of fungi that cause tree decay and wood decay. The properly formulated CCCSNs treatment can be used to treat trees and commercial wood products to increase their decay resistance.

Our *in-vitro* test against Southern pine beetle associated blue stain fungus (***Ophiostoma Minus)*** shows that proper formulation of CCCSNs possesses a strong antifungal property (Figure 7). Southern pine beetle associated blue stain fungi are the number one natural enemy that causes huge destruction to loblolly pine and other southern pines, all of which are key commercial species for timber and forest product industries. Properly formulated CCCSNs treatment can be used to treat pine seedlings during planting and mature trees to increase their pest resistance against the blue stain fungi.

In Southern USA, Formosa subterranean termites (*Coptotermes formosanus)* are particularly destructive to residential homes that are made of wood. Current industrial treatments have come under attack when toxic elements such as arsenic are used. There is a great need to develop and to test new chemicals for wood-based treatments for safely securing residential structures. Our research has shown that wood treated with CCCSNs is highly resistant to Formosa subterranean termite attack (Figure 8). Actual copper content in CCCSNs treated wood is less than 0.25wt%, which is significantly lower than the copper content of commercially ACQ treated wood. The CCCSNs treatment can be used as a viable and environmental friendly alternative for wood treatment against Formosa termites and decay fungi.

Figure 6. Wood treated with CCCSNs shows remarkable decay resistance against white rot fungus, *Trametes versicolor*, after 16 weeks of testing based on AWPA E10 Method (for Decay test).

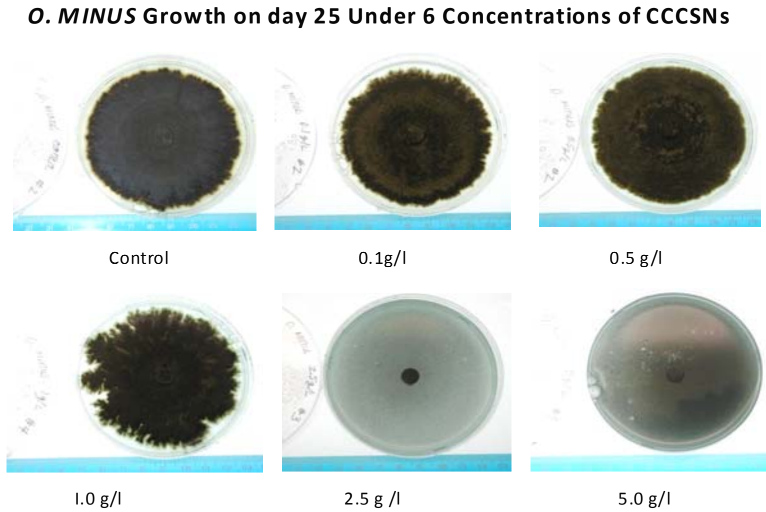
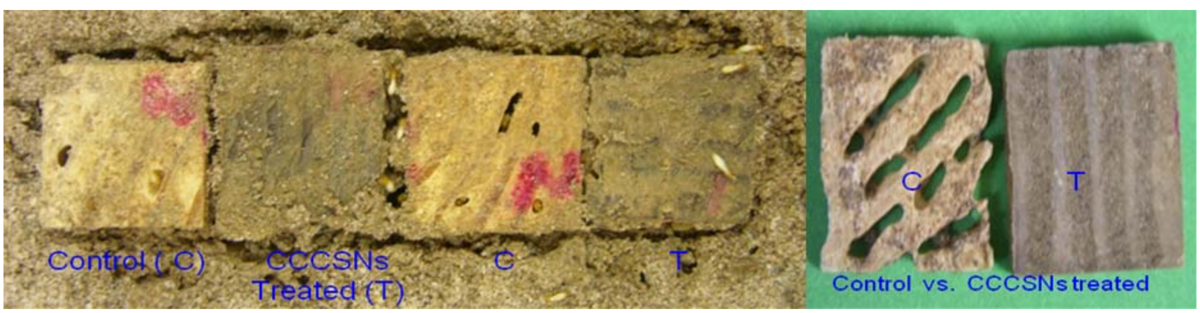


Figure 7. *In-vitro* test against Southern pine beetle associated blue stain fungus (*Ophiostoma Minus)* shows that the CCCSNs formulations at 2.5g/l and 5.0g/l possess a strong antifungal property.



Formosa Termite test: control (C) shows significant termite damage

Figure 8. Wood treated with CCCSNs is highly resistant to Formosa subterranean termite attack. The test was conducted based on the AWPA E1 Method (for Termite).

Summary

Our research has shown that CCCSNs as a new generation of environmentally friendly nanomaterial will have a great potential to be used for forest protection against decay fungi, blue stain fungi, and Formosa termites. This joint effort formed by Southern University, Louisianan State University and USDA-FS will significantly advance research on Southern pine beetle associated blue stain fungi and other important forest pests. Our long-term goal is to develop safe and effective formulations and treatment strategies for commercialization through industrial partnerships that use nanotechnology to protect our forest and forest products. This effort will lead to development of new nanotechnologies to protect forest products against woody decay and termites, thus, helping secure our natural resources and economy. This research may have broader applications in pest control in the field of Agriculture.

Acknowledgements

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Introduction

- Nano-materials have generated tremendous interests because they offer many opportunities to deliver unprecedented material performance.
- As a new generation renewable nano-material, the **Copper-Carbon Core-Shell Nanoparticles (CCCSNs)** have received increasing attentions because of their low cost, unique stabilities, and demonstrated performance against Formosan termite and fungal diseases.
- The goal of our research is to develop safe and effective formulations and treatment strategies in using nanotechnology for forest and forest product protection.

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On-going research activities

- (1) characterization of physical and chemical properties of CCCSNs and their interactions with environment;
- (2) examination of CCCSNs uptake/distribution patterns within seedlings and mature trees and the effect on plant physiology, growth and development;
- (3) investigation of the effects of CCCSNs on southern pine beetles and associated fungi, wood rotten diseases, and Formosa termites that attack living trees and wood products.

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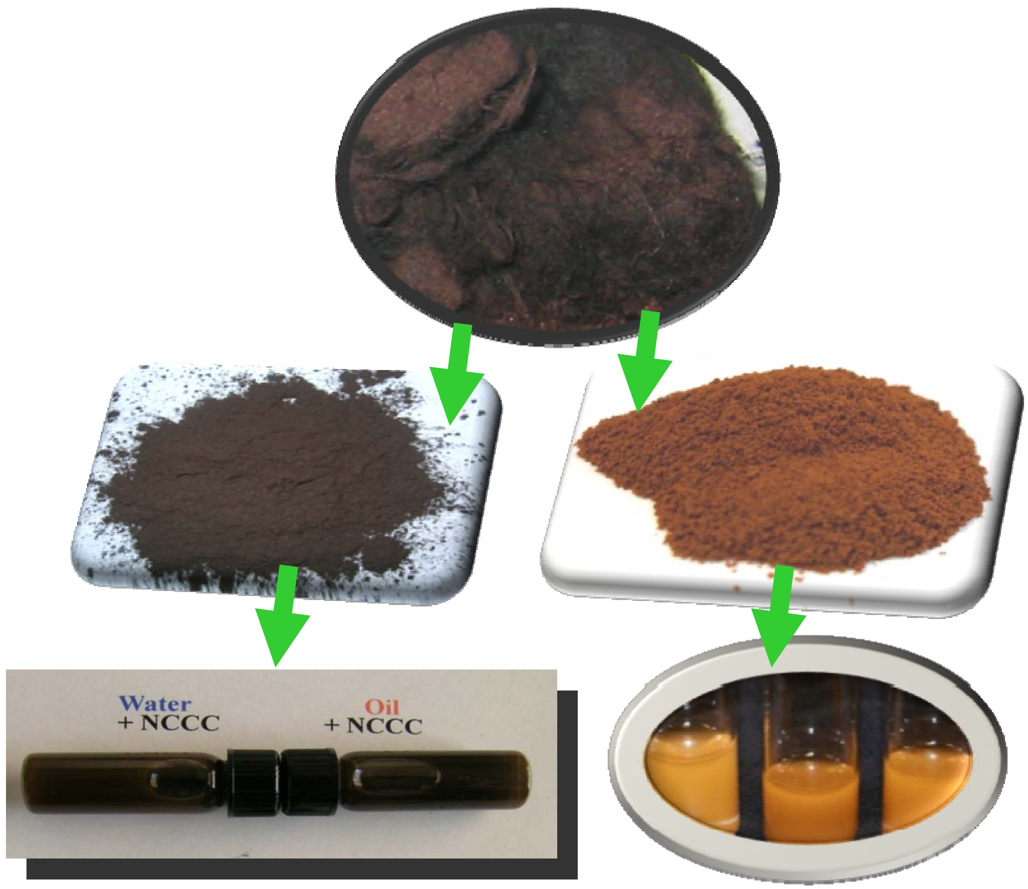
CCCSNs Characterization

Patented Technology to Make Metal-Carbon Core-Shell Nanoparticles by Using Natural Fiber as Templates (US Patent Pending 60/772.325)



CCCSNs contain carbon black from cellulosic material and yellow powders

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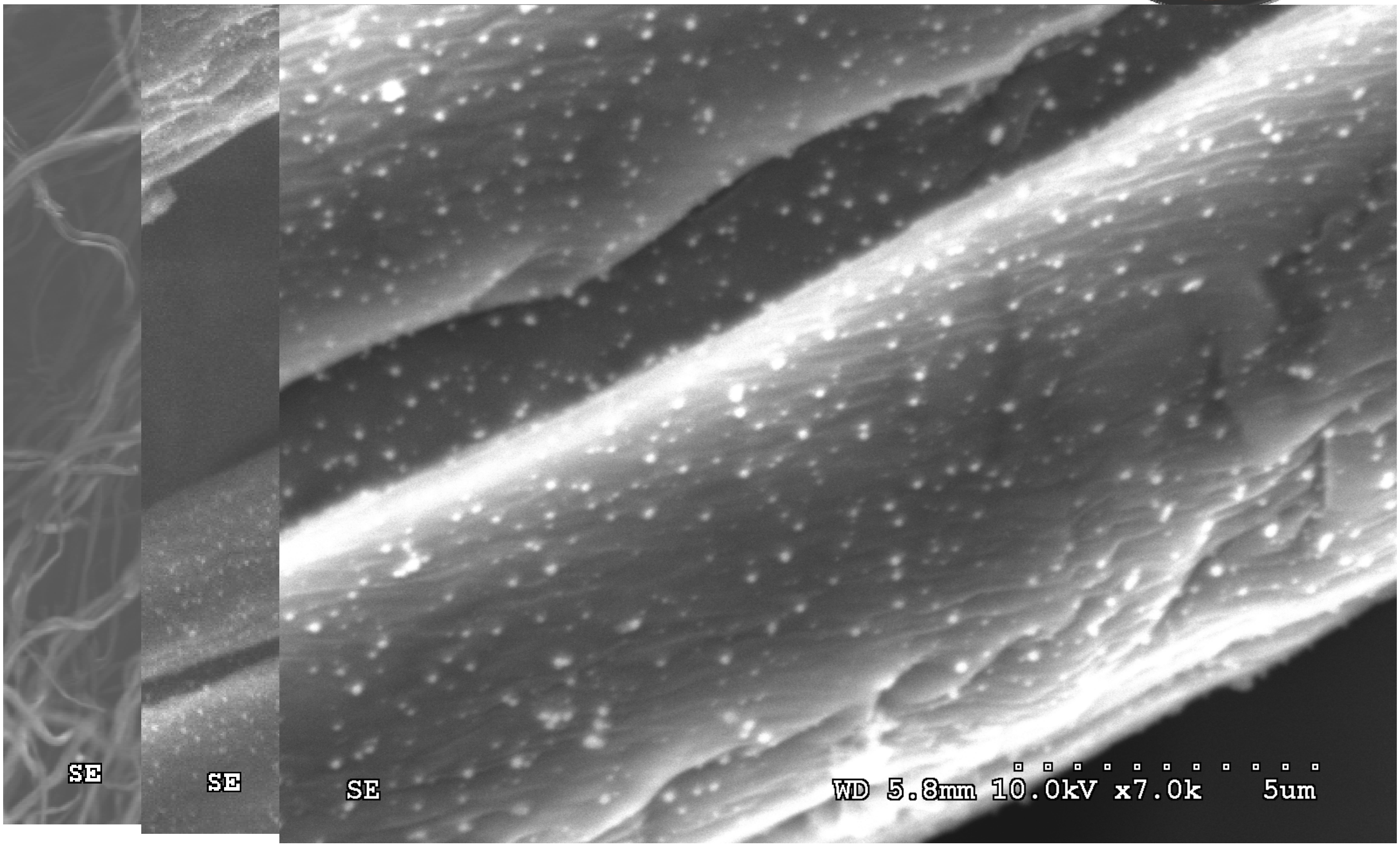
SEM Images of CCCSNs Raw Material Made by Using Cotton as Templates



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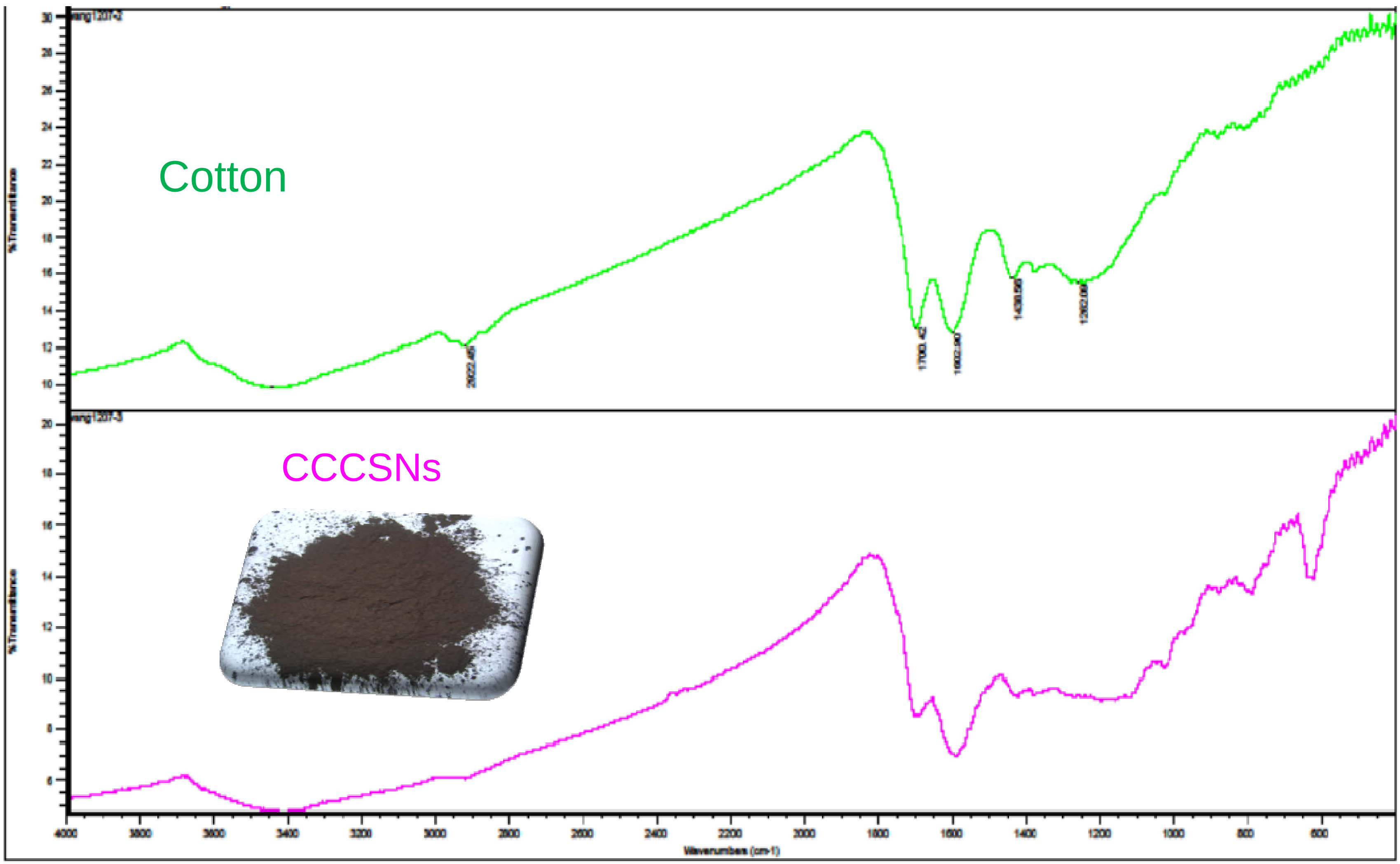
FTIR Shows Functional Groups Retained in CCCSNs are Similar to Those in Cotton Fiber



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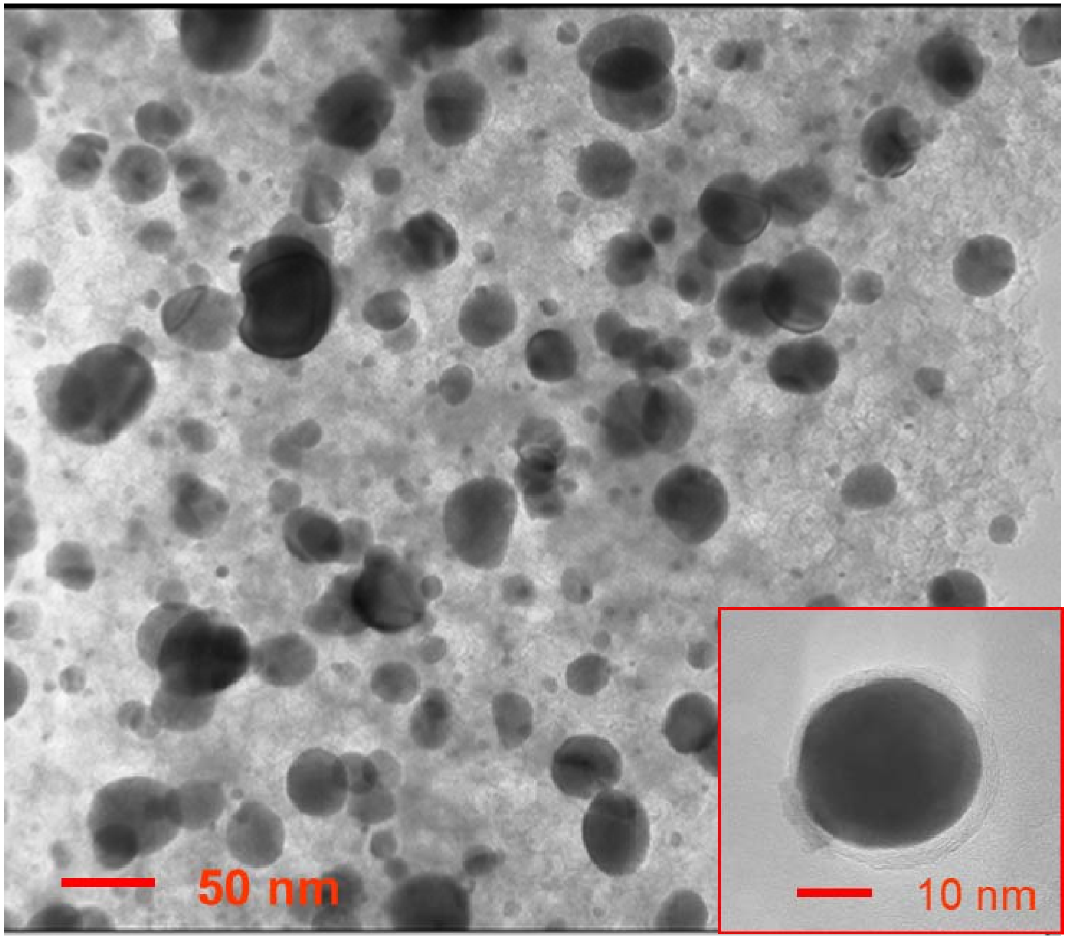
TEM of Fabricated CCCSNs



- TEM micrographs show CCCSNs are embedded in the porous carbon black substrate;
- The core shell structure is formed during the one step fabricating process;

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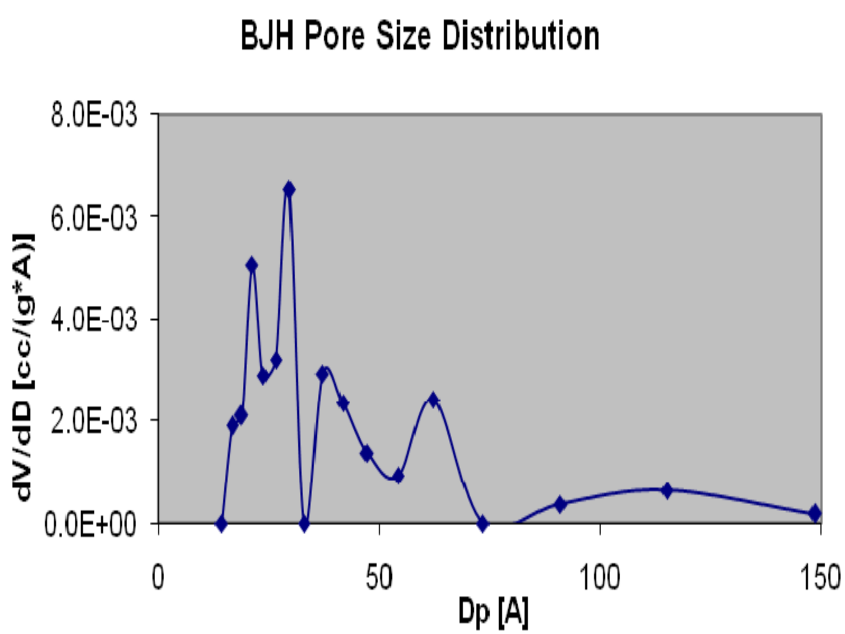
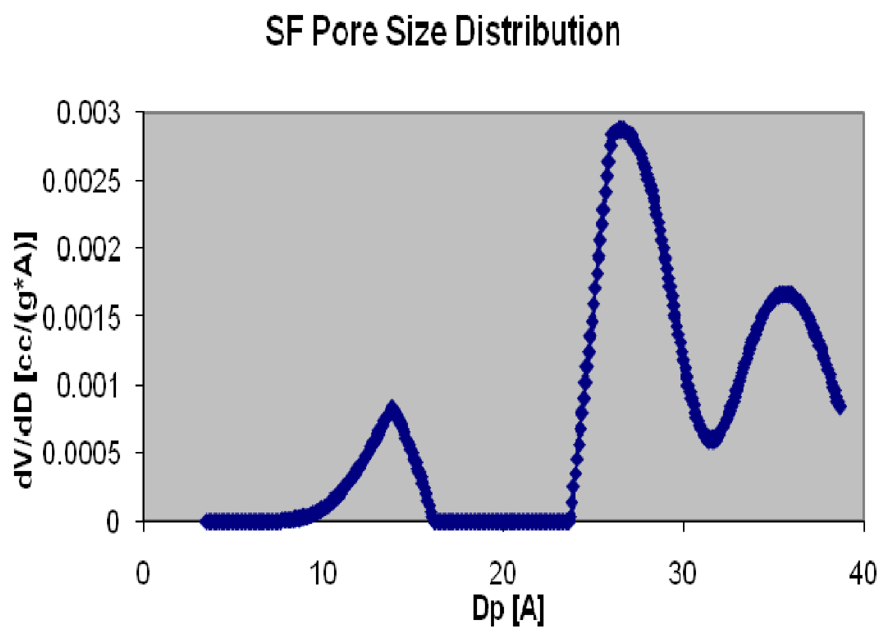
CCCSNs Shell Surface Properties

CCCSNs are actually fairly porous with a decent surface areas of 70-100 m^2/g, internal pore volumes of 0.11- 0.16 cm^3/g, and an average pore size ~3 nm





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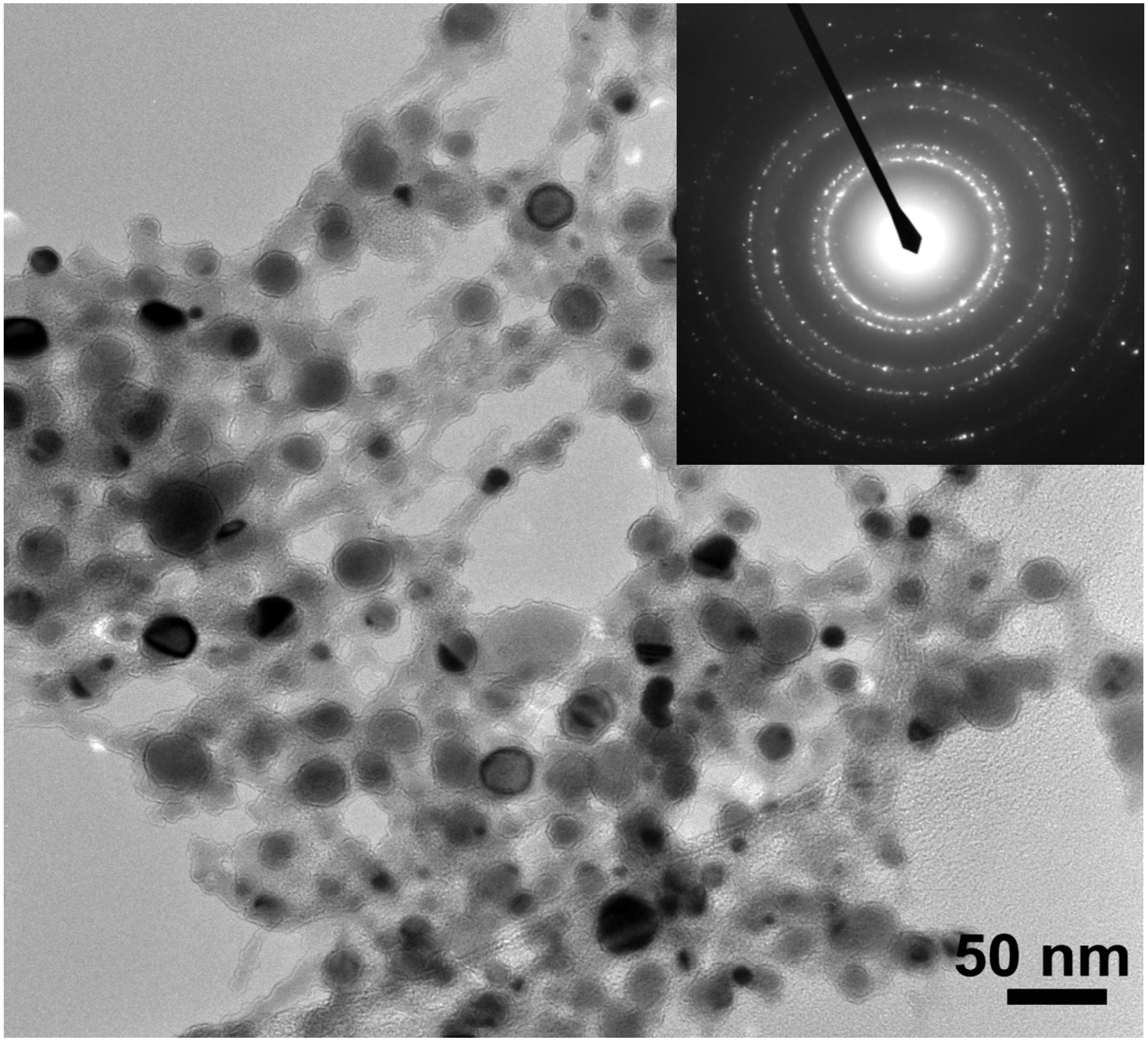
TEM and X-Ray Diffraction of CCCSNs Structure



- TEM image of CCCSNs after 36 months of immersion in water under ambient atmosphere. **Inset**: X-ray diffraction shows no change to the nanoparticles' copper cores after this 1.5 year environmental exposure

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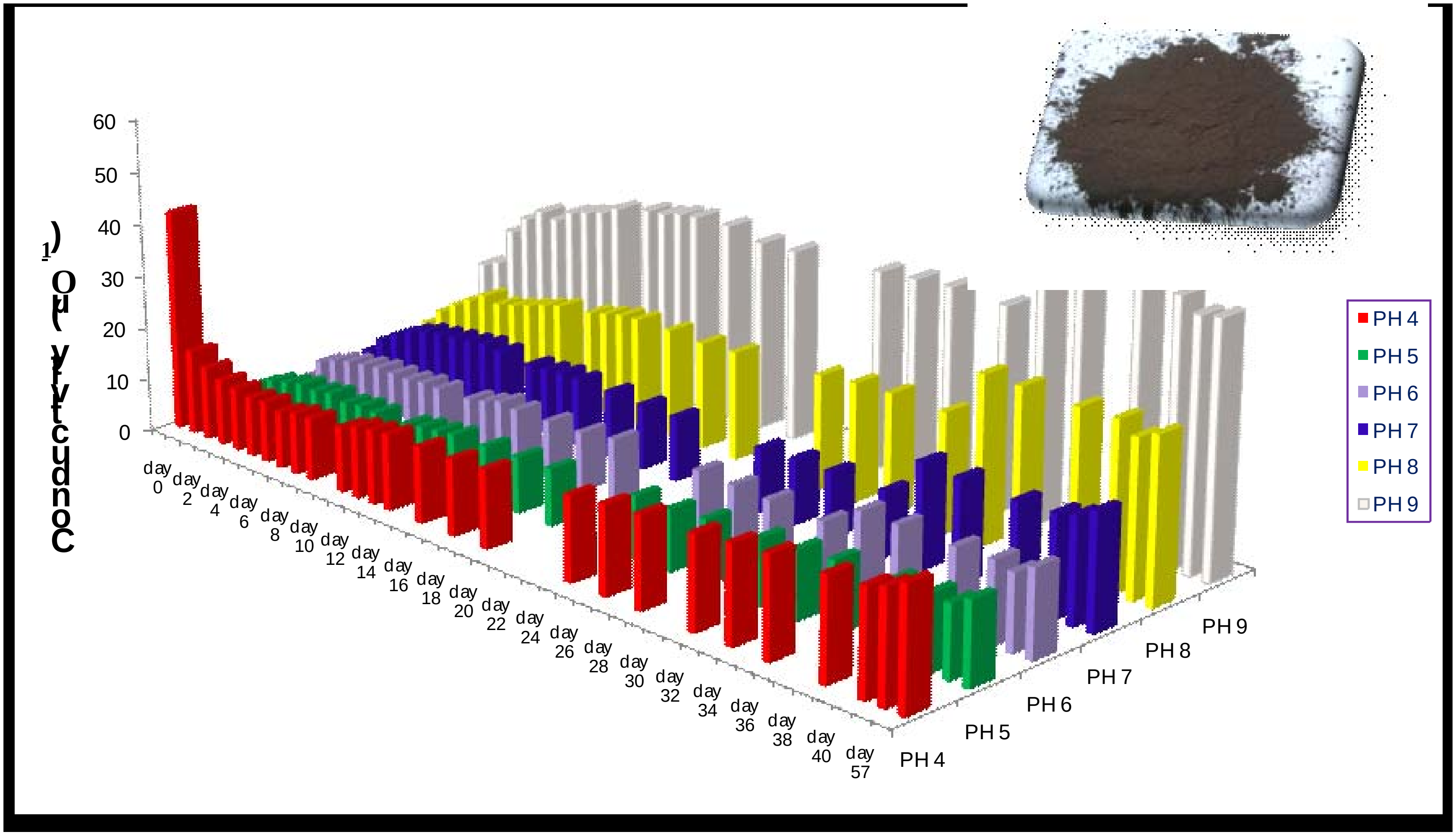
CCCSNs possess good chemical stability



Conductivity as a function of immersion time of carbon black powder containing CCCSNs in the different pH solutions.

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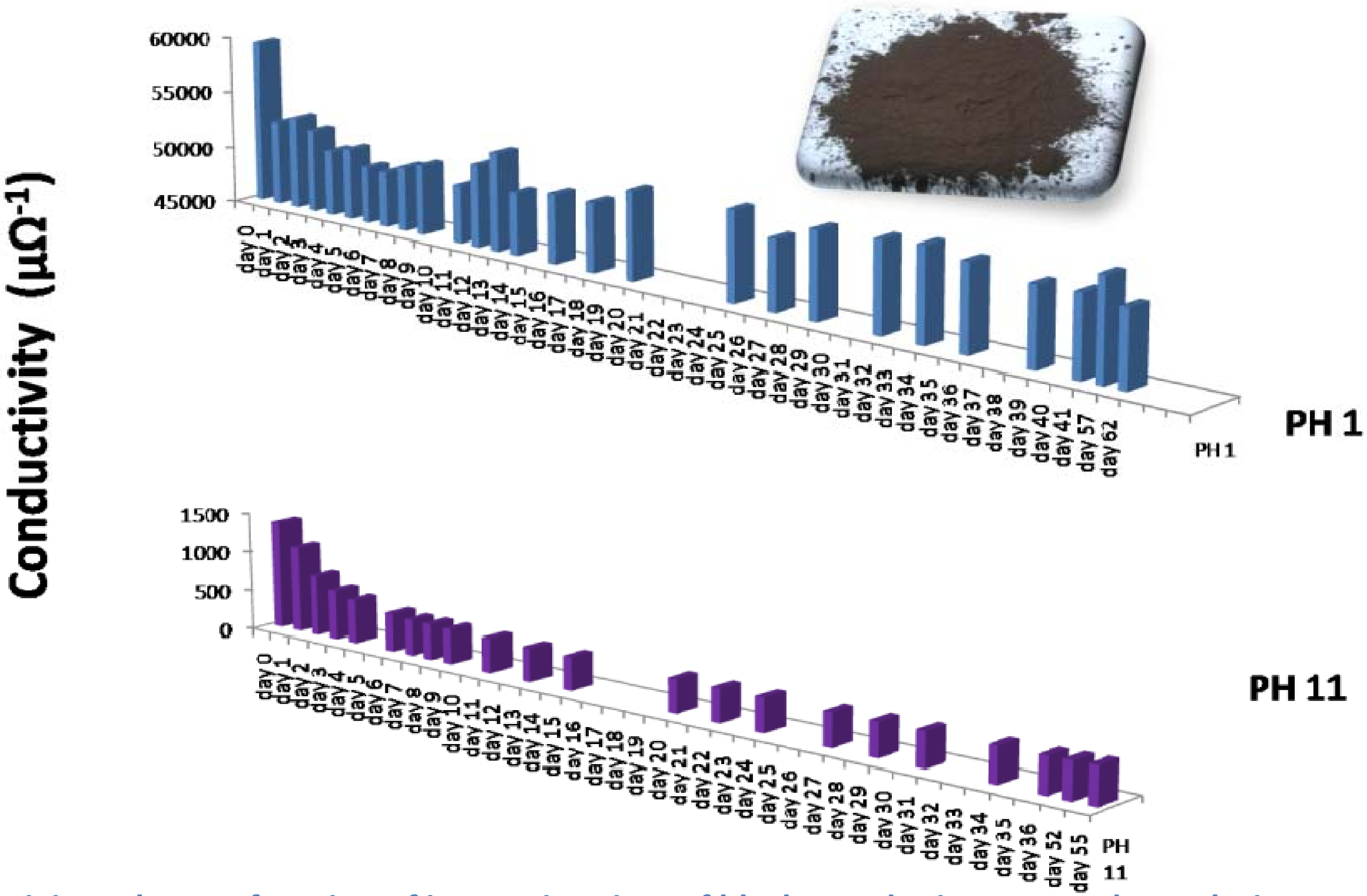

Conductivity values as function of immersion time of black powder in pH=1 and 11 solutions

Both Figs indicated that CCCSNs did not release significant amount of Cu^{++} and Cu^{+} ions in the testing solutions. Since the plant healthy are mostly sensitive to copper ions, the CCCSNs lethal effect to plants by release copper ions can be ignored.

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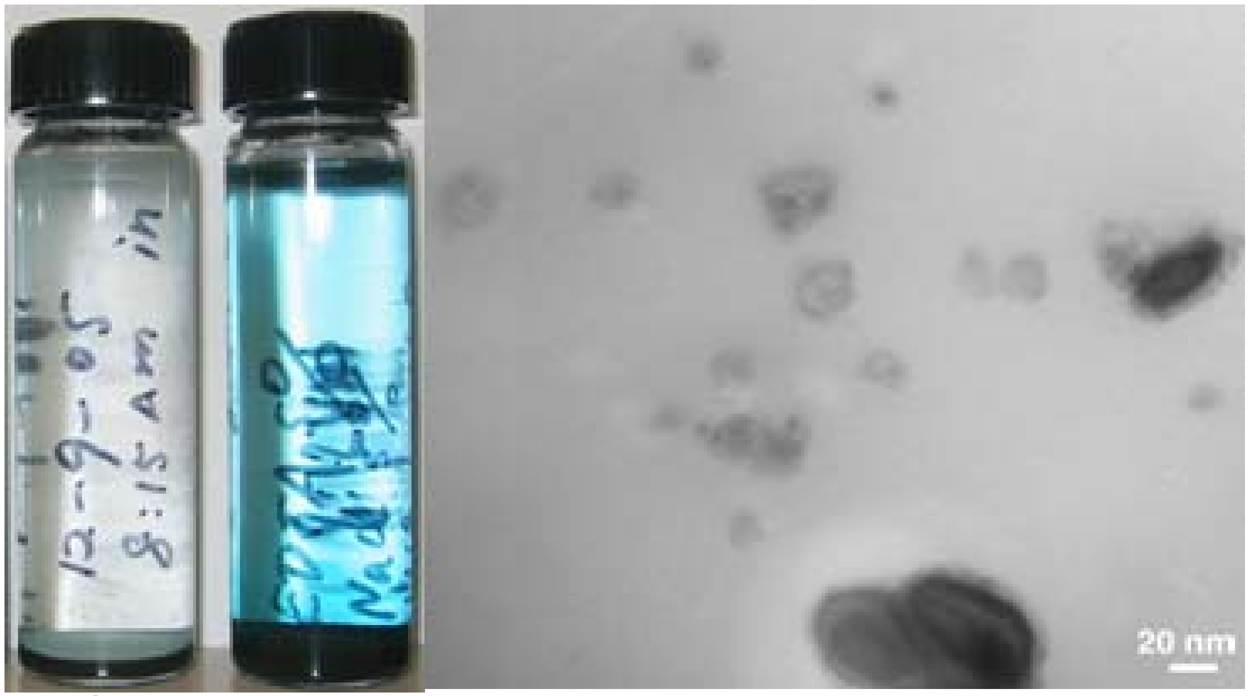
CCCSNs Metal Core Interactions with NaCl and EDTA



NaCl NaCl+EDTA

72 hours immersion test . *left bottle:* 3 wt% NaCl solution; *right bottle*: 3 wt% NaCl + 5 wt% EDTA. The TEM image shows empty carbon shells after 72 hours immersion in the solution with EDTA.

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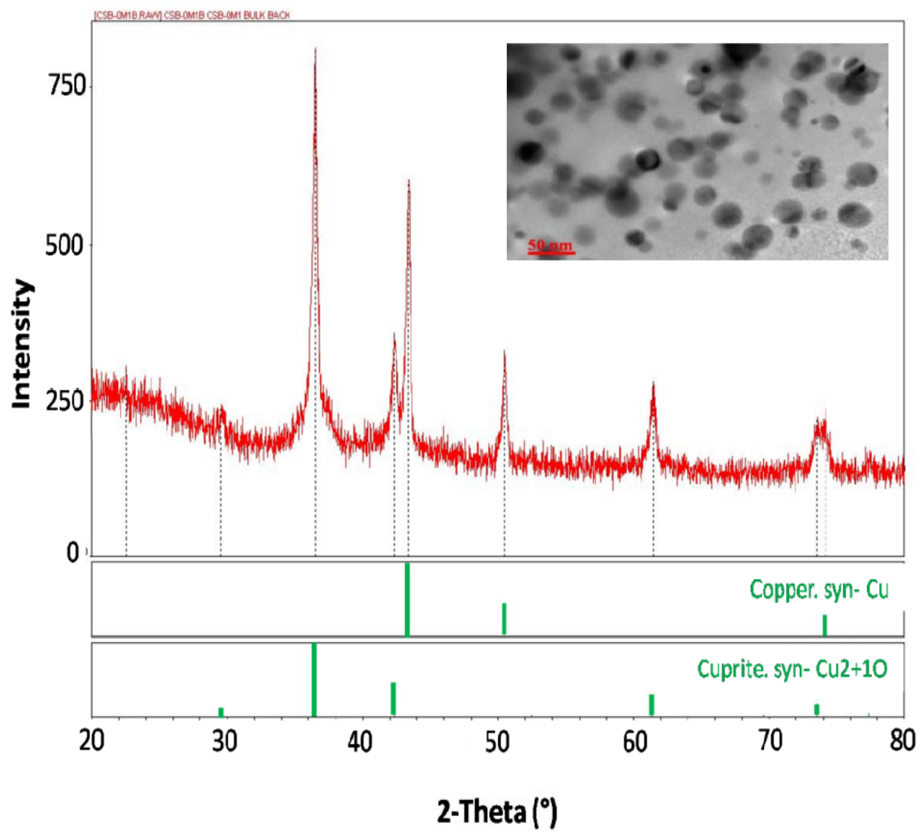
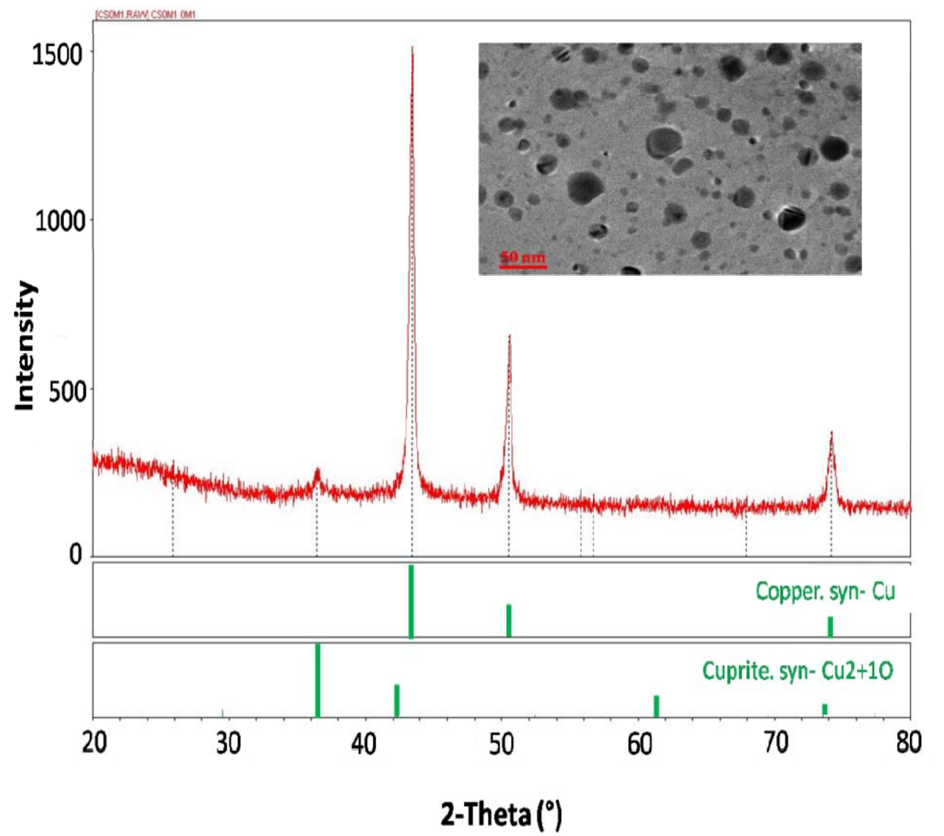
CCCSNs Can Be Regenerated from Oxidized State by Heat Flash





40 min in water + air; 30min dry in vacuum over at 60 ° C.

CCCSNs form a balanced Cu_2O-Cu system after oxidation

40 min in water + air, 30min dry in vacuum over at 60 ° C and plus heat flash at 360 °C in N_2 environment.

CCCSNs regain the original structure after a heat flash

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Biological applications of CCCSNs

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CCCSNs Treatment in Loblolly Pine

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Loblolly Pine Experiment

Experimental site	Southern University Ag Center Urban Tree Farm, Baton Rouge, LA 70813			
Tree Age	10 years old			
Treatment type	control	CCCSNs	CuO	Cu_2O
Application rate, raw material per tree	NA	4 g	3.75g	3.41g
Pure copper content in raw material	NA	1.6g	3g	3g
No. of trees per treatment	4			
Application method	Injection at DBH level			
Date of injection	28-May-10			
Date and location of wood core sampling	2-June-10, 1 week after injection, Samples taken at 1 feet above the injection point			
	28-June-10, 4 weeks after injection, Samples taken at 2 feet above the injection point			
Sampling device	Increment Borer			

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Sampling of wood core

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Wood Core Exposure Study

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Wood Core Exposure Study

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Wood Core Exposure Study

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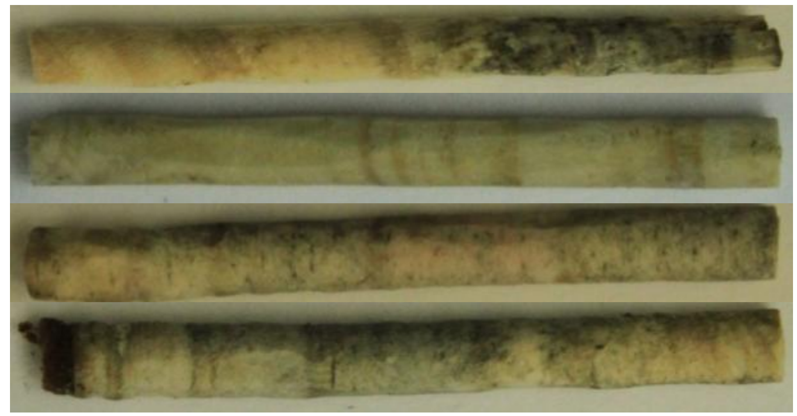
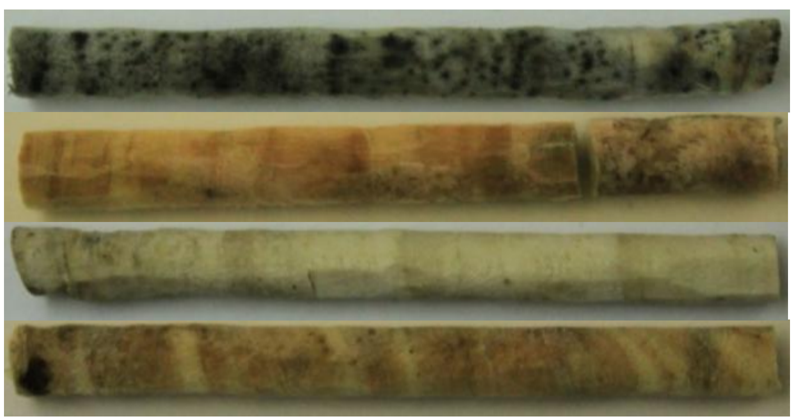
Wood Core Decay Test Indicated CCCSNs Treated Loblolly Pine Wood Possesses Antifungal Property

Control

CuO



Cu_2O



CCCSNs

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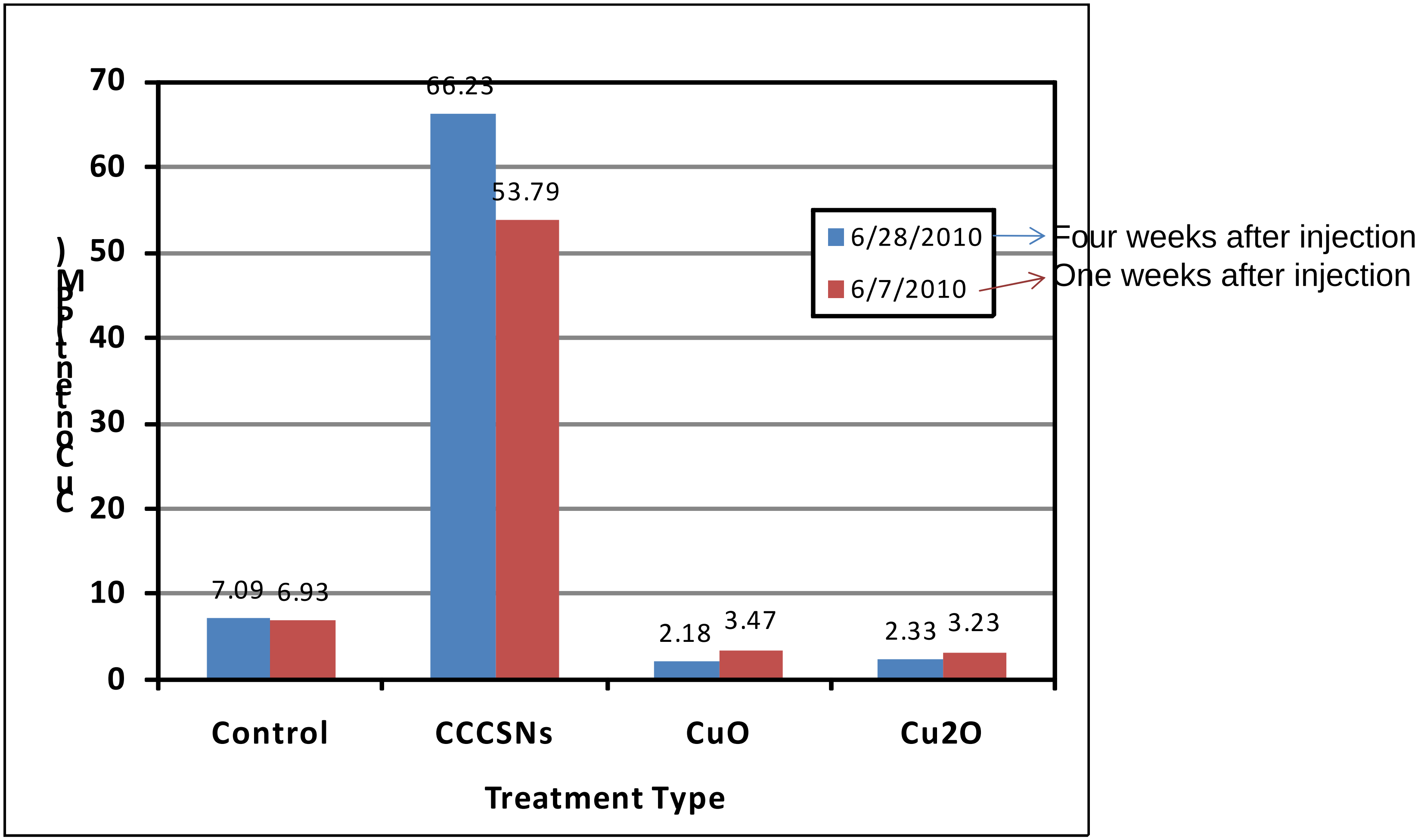
CCCSNs uptake in main trunk of 10 yr old loblolly pine



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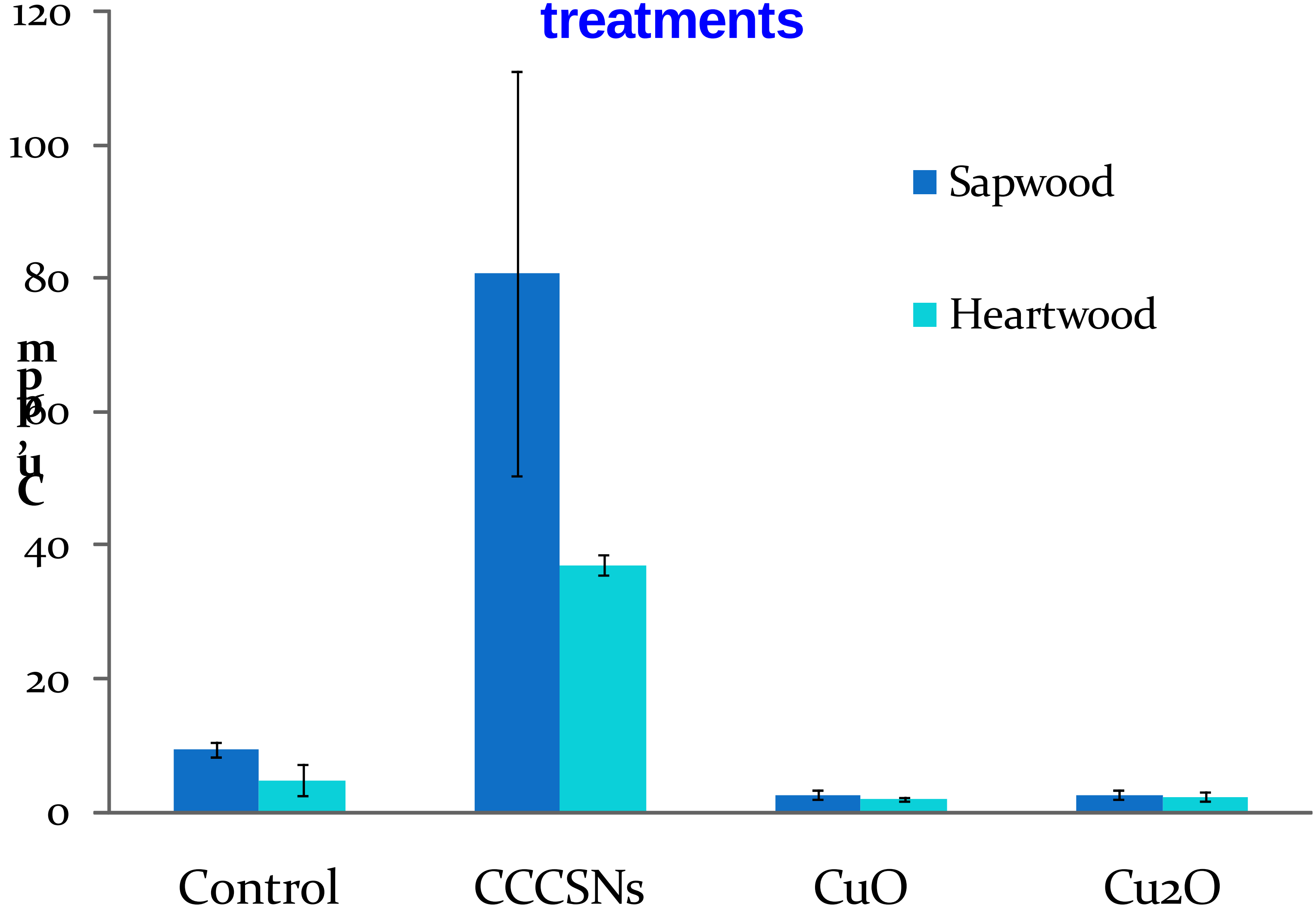
Copper Content in sapwood and heartwood of 10-year-old loblolly pine after 4 weeks of treatments



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Effect of CCCNPs on Baldcypress Seedlings

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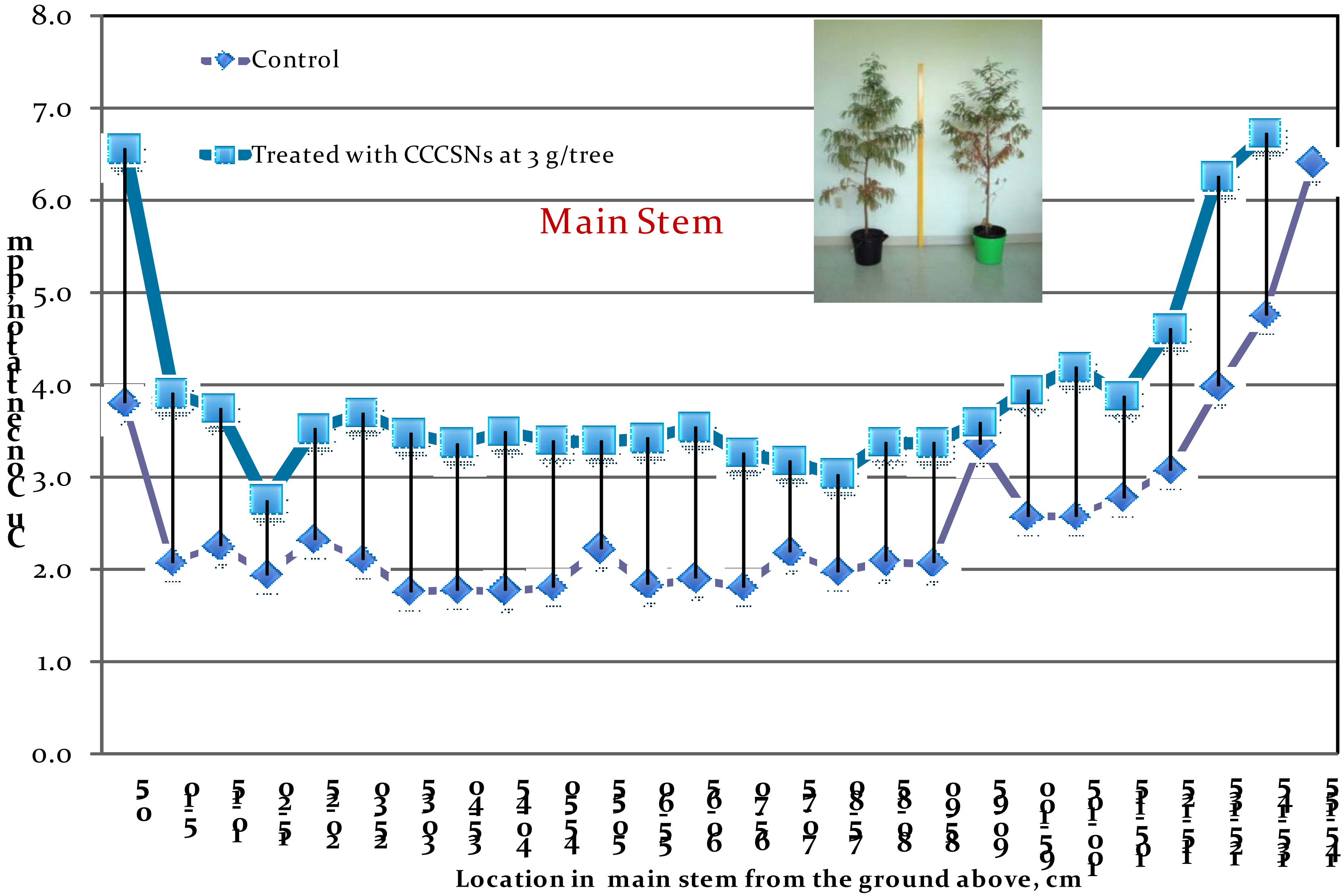
CCCSN s uptake along the main stem of a 2-year-old baldcypress after 25 weeks of CCCSNs treatment



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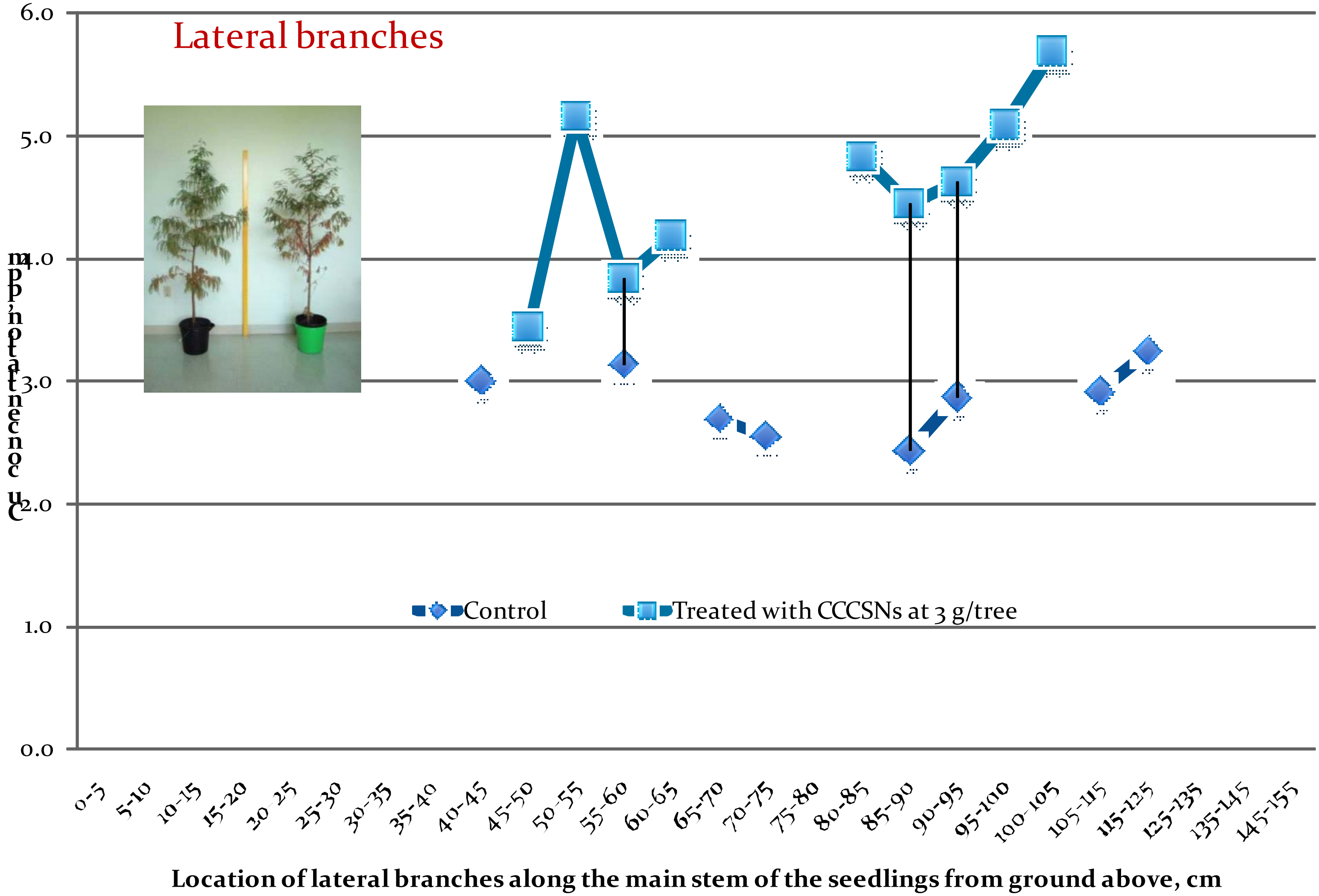
CCCSNs uptake in the lateral branches of a 2-year-old baldcypress after 25 weeks of CCCSNs treatment



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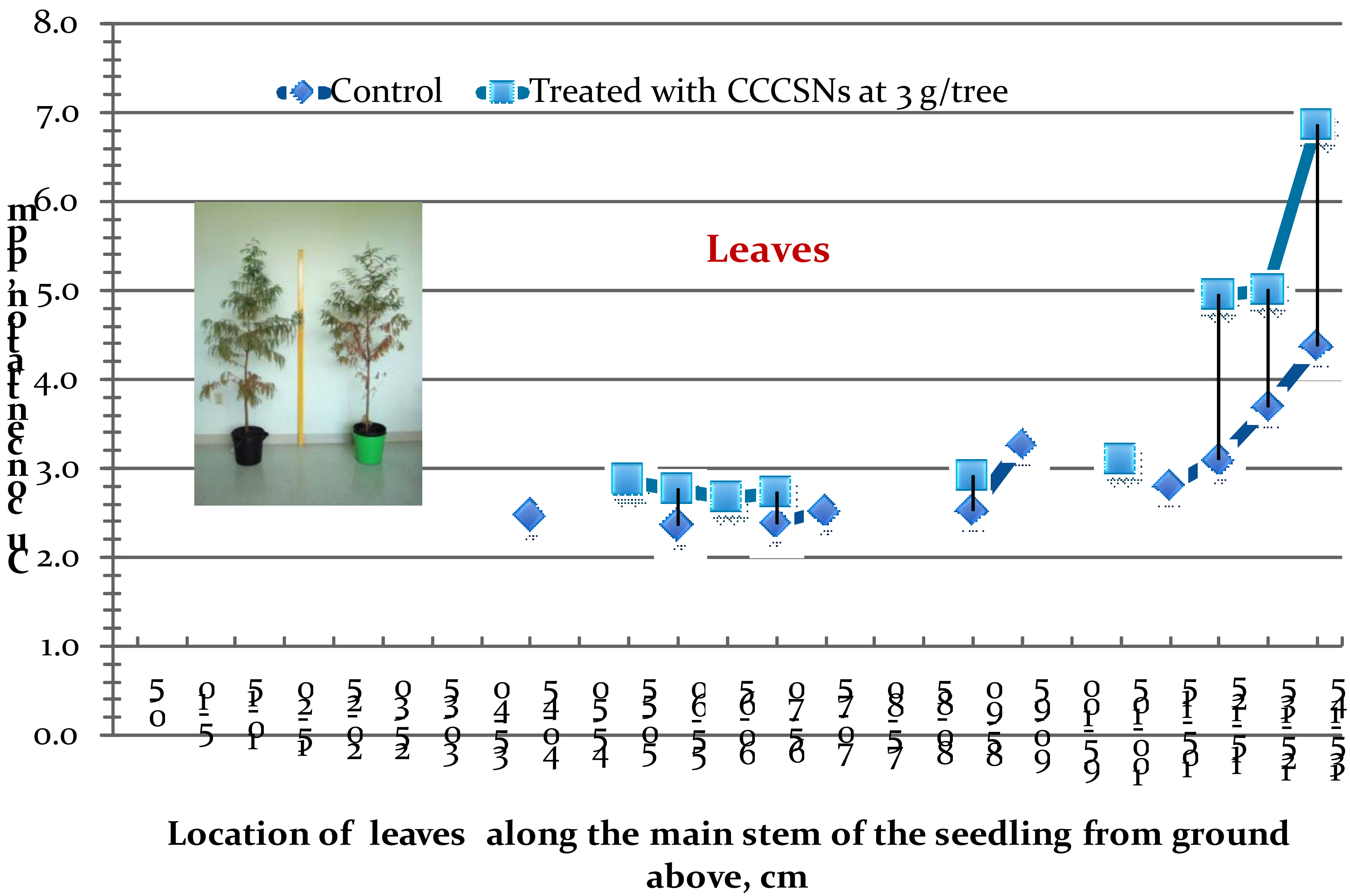
CCCSNs uptake by leaves of a 2-year old baldcypress after 25 weeks of CCCSNs treatment



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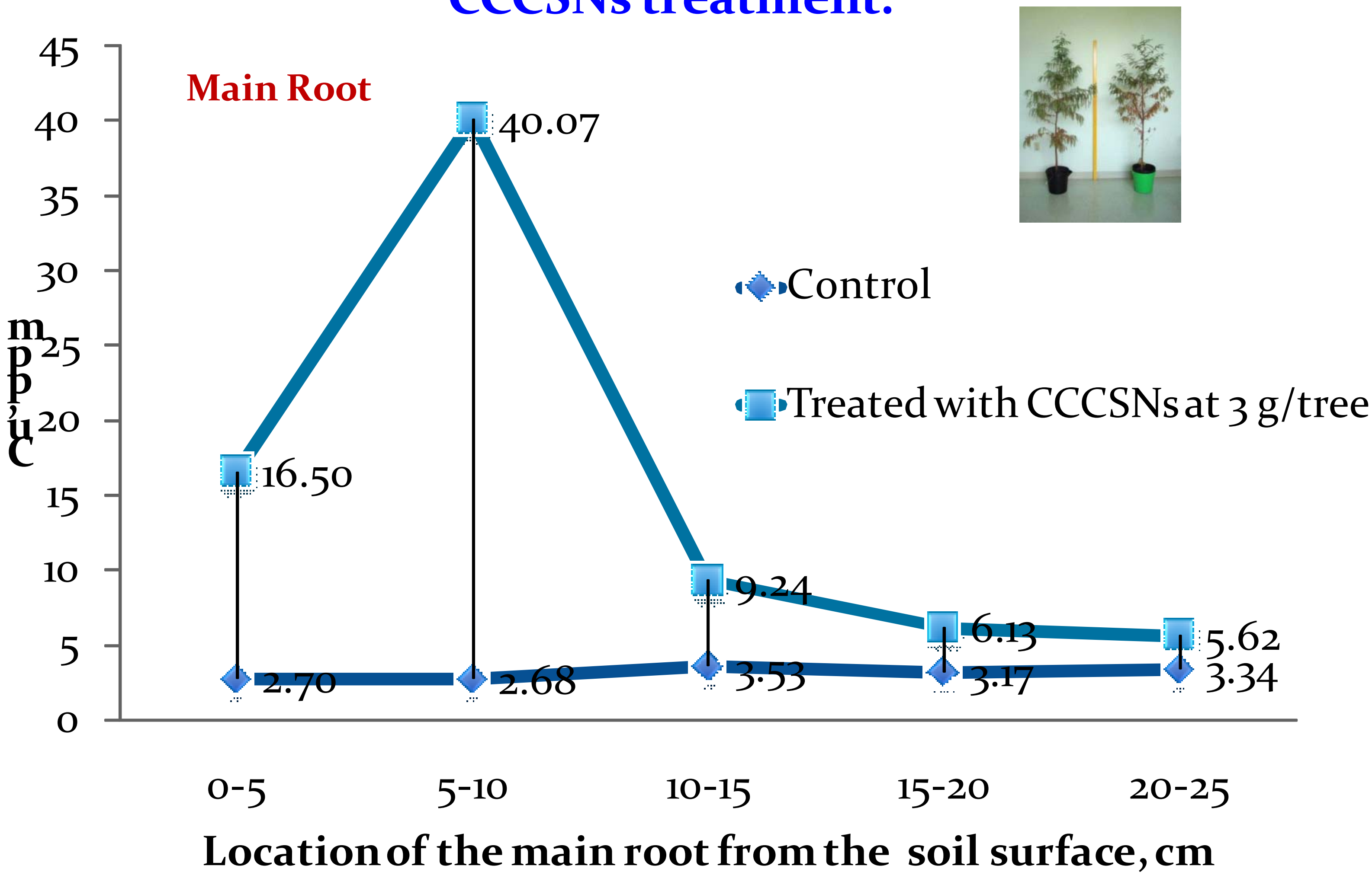
Copper distribution in different sections of the main root of 2-year-old bald cypress seedlings grown in 2-gallon containers after 25 weeks of CCCSNs treatment.



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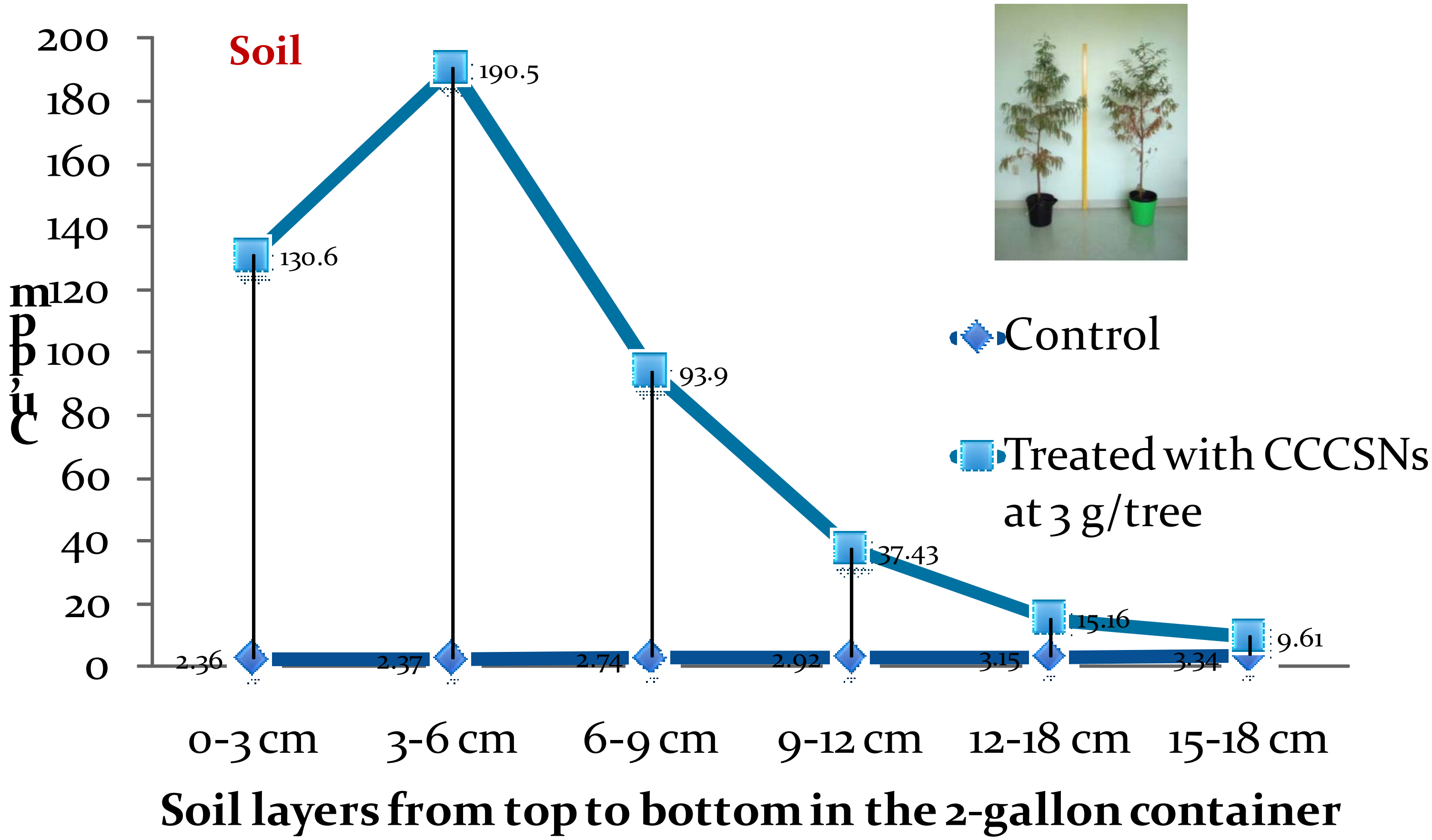
Copper distribution in different layers of the soil of 2 year -old containerized bald cypress seedlings after 25 weeks of CCCSNs treatment



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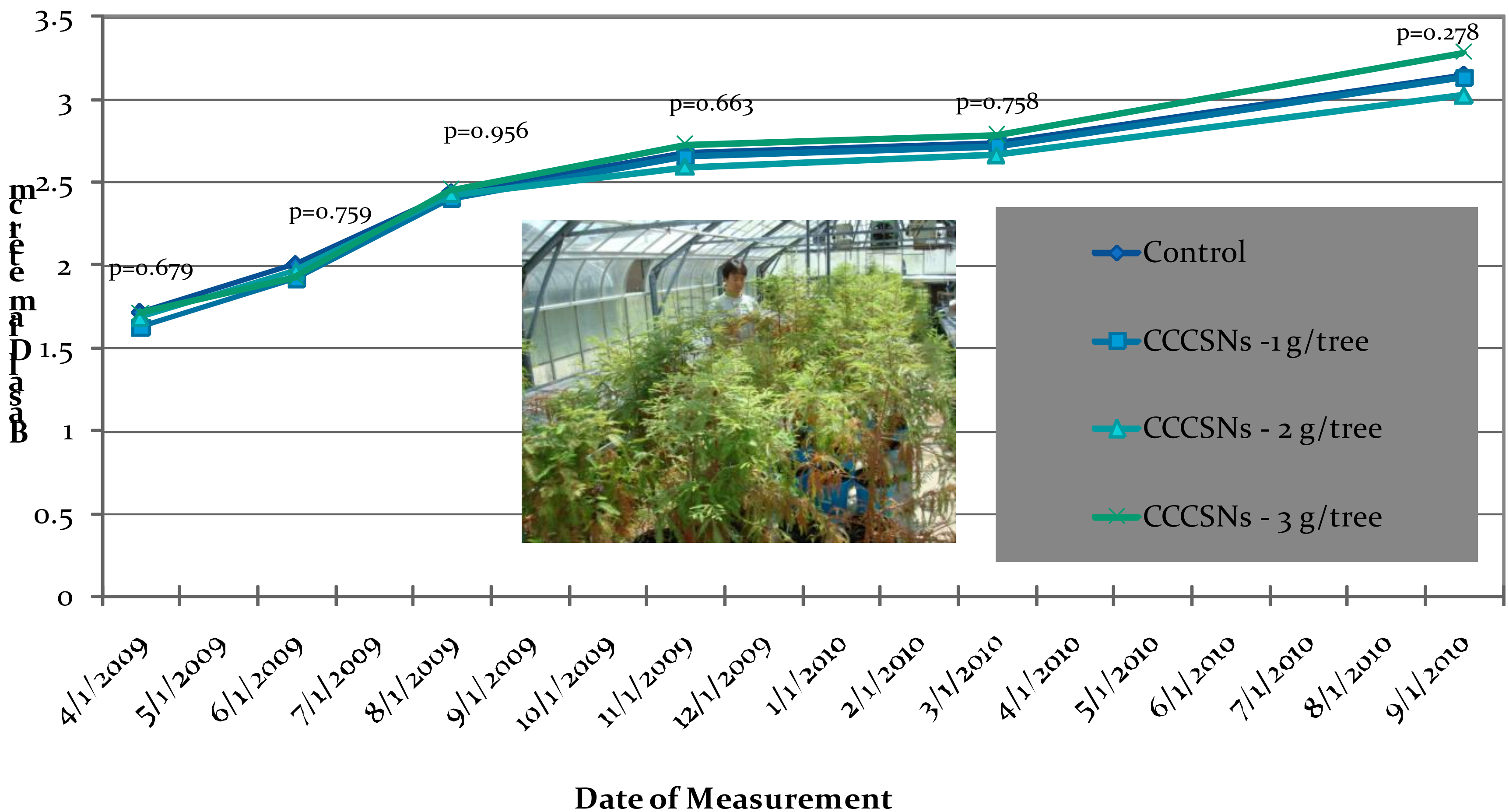
Diameter growth of 3-year-old bald cypress during a course of 16 months of CCCCSNs treatments - show no significant difference among the treatments



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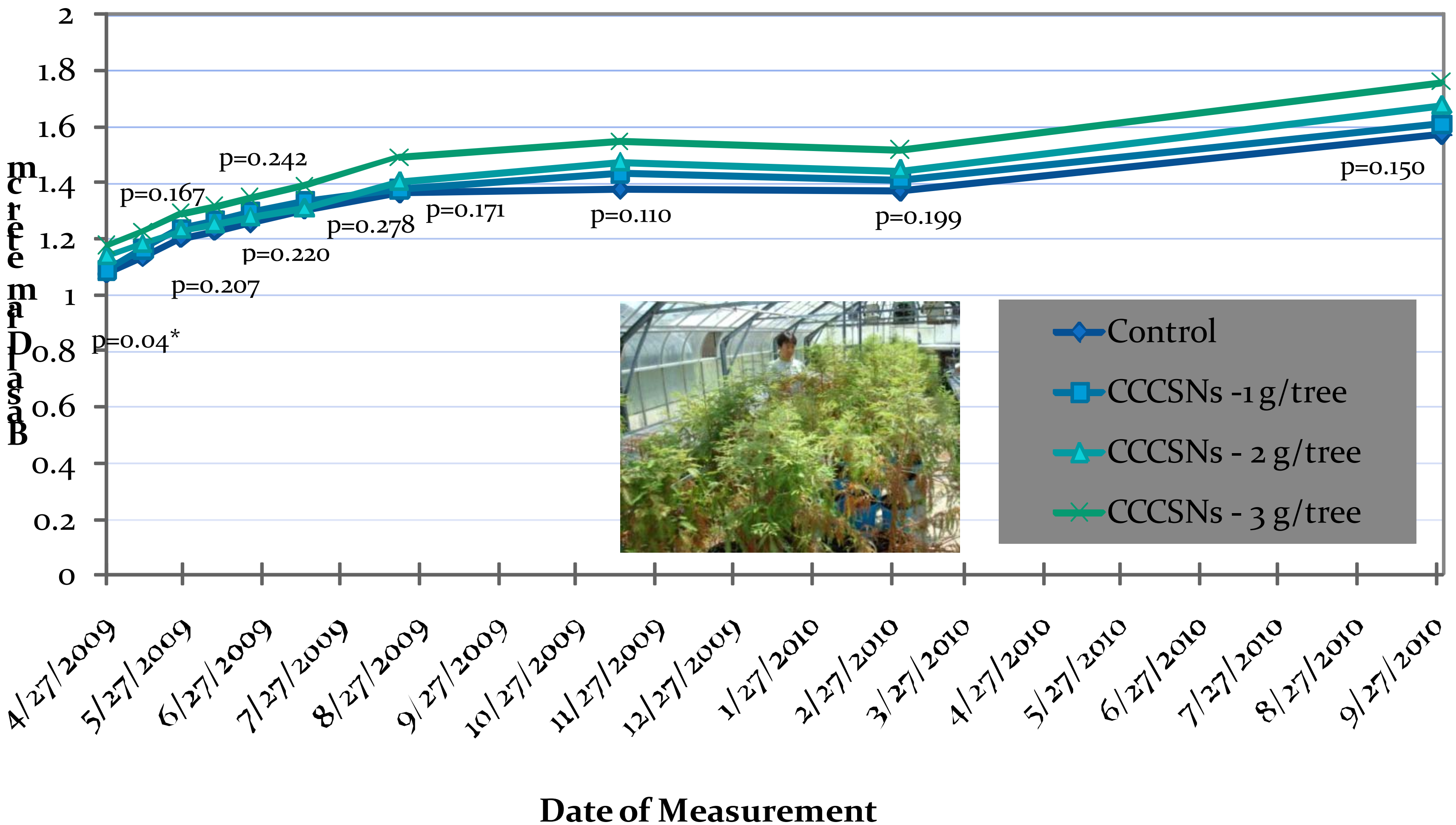
Height growth of bald cypress seedlings during a 16-month course of CCCSNs treatments



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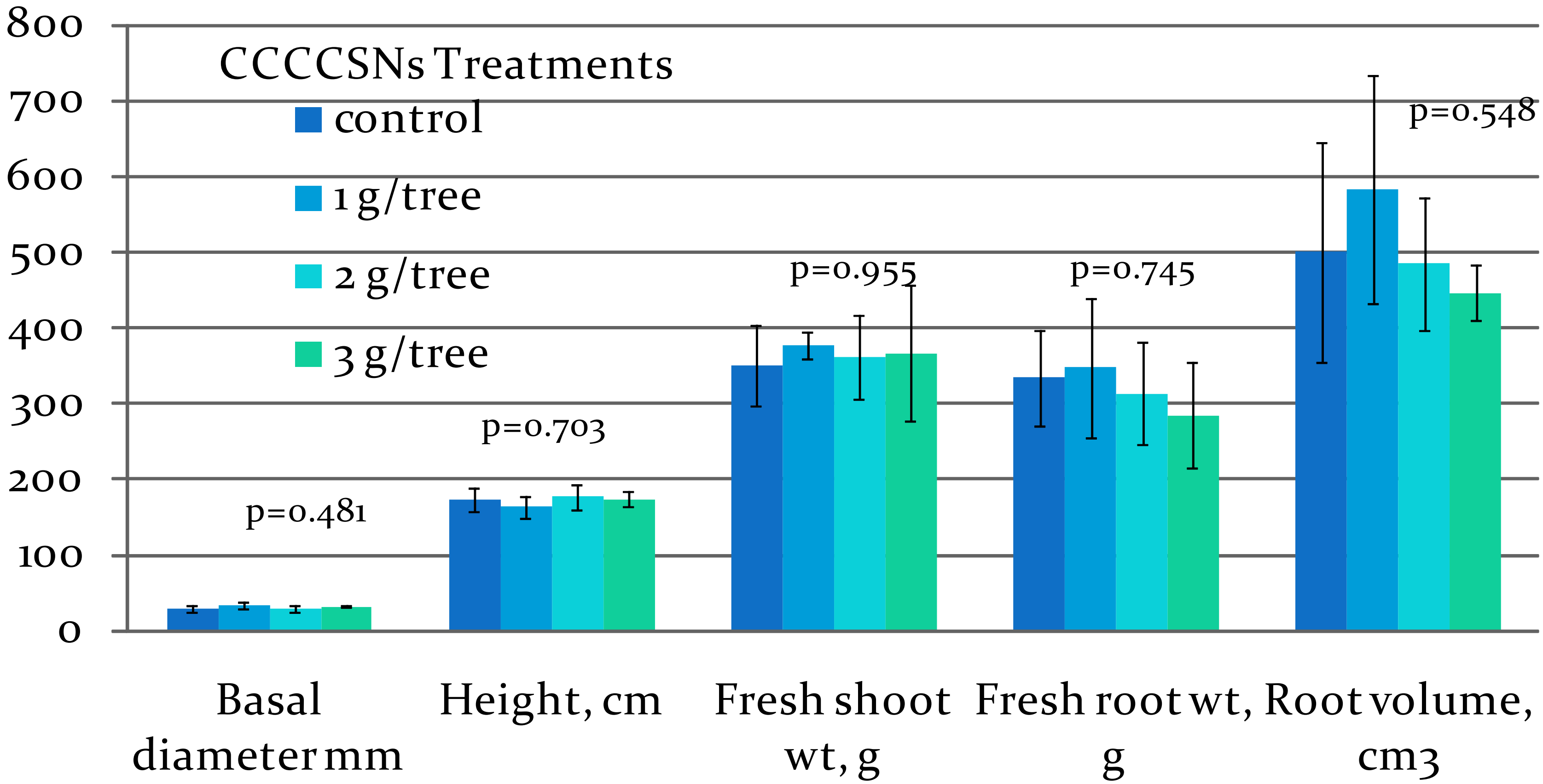
Baldcypress growth and biomass study after 20 months of CCCCSNs treatments – Show no significant difference among the treatments



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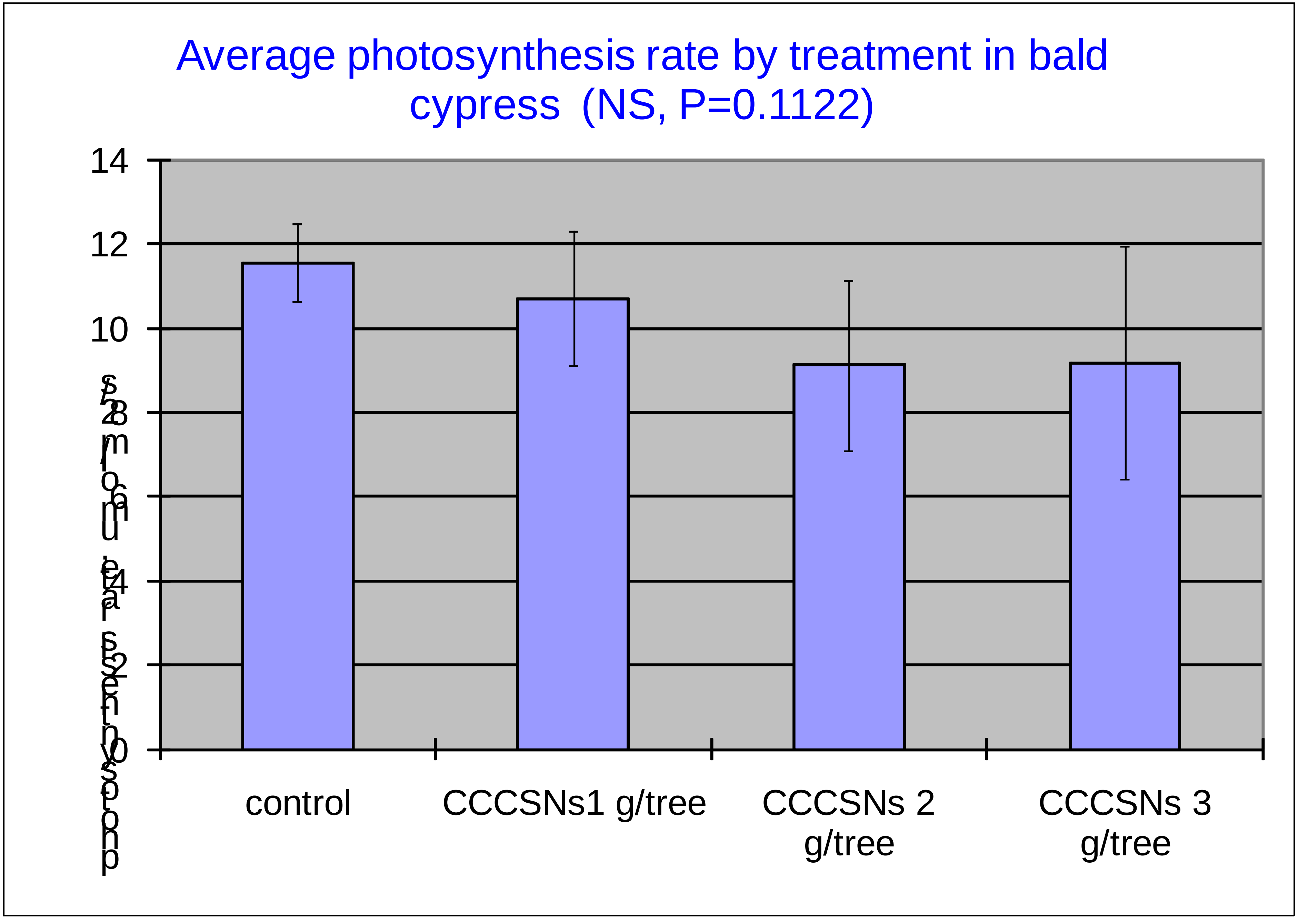

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Effect of CCCSNs on Southern Pine Beetle and Associated Blue stain Fungus

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Southern Pine Mortality in Urban Area

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Southern Pine Beetle Associated Blue Stain Fungi – Showing the Progressive Attack on Pine Tree

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Antifungal Activities of CCCSNs against Blue stain Fungus

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Blue Stain Fungi Inoculation and Measurements

Pure culture of blue stain fungus, *O. Minus* was obtained from USDA-FS Pineville Pathology Research Lab.

The fungus were re-cultured for 10 days before inoculation.

CCCSNs concentrations of 0 (control), 0.1, 0.5, 1, 2.5 and 5 g/L were incorporated into autoclave-prepared malt extract agar (MEA) media (3.5% MEA in water), after the agar cooled to 50^{o}C.

The mixing was done in an ultrasonic water bath. The mixed agar was poured at 20ml per Petri-dish (12mmx85mm internal dimension).

The blue stain culture (9mm disc) was inoculated onto the agar media in Petri-dishes with four replications per concentration.

The media was incubated in an incubator at 25 degree C darkness.

The mycelia growth was measured daily for at least 30 days.

The fungal colony was photographed every other day under a positive flow culture chamber.

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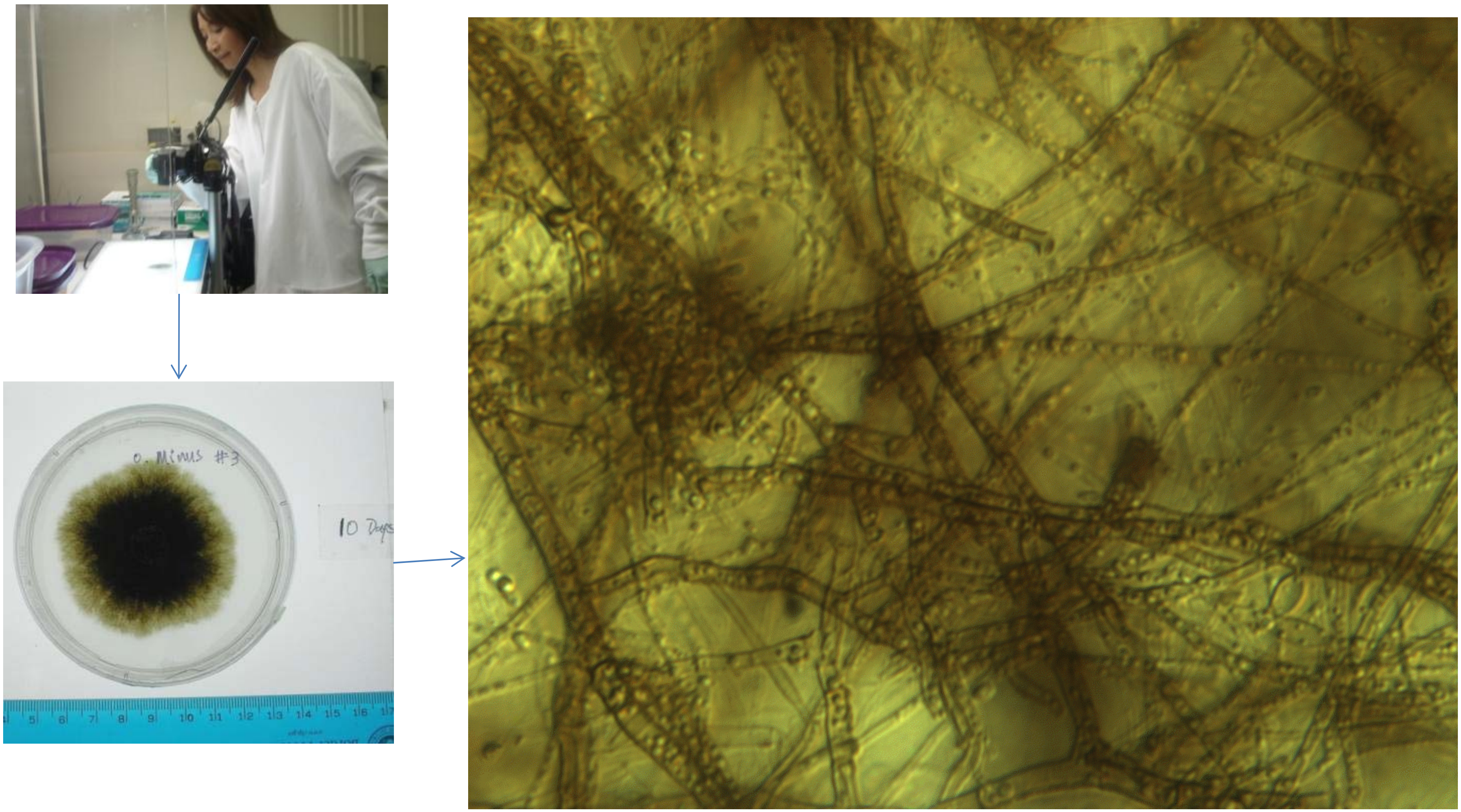
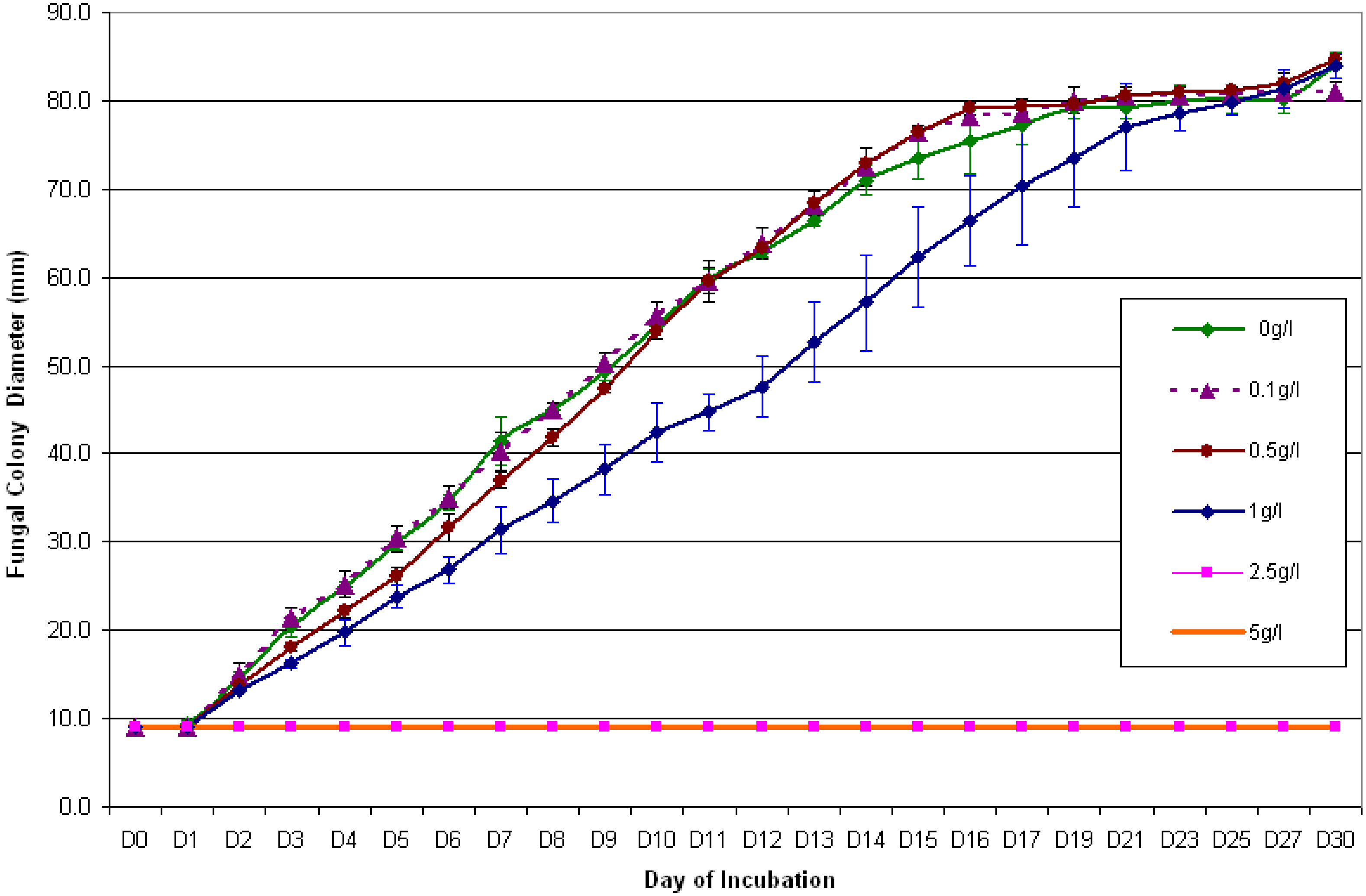
Blue-Stain Pure Culture, *Ophiostoma Minus*



Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

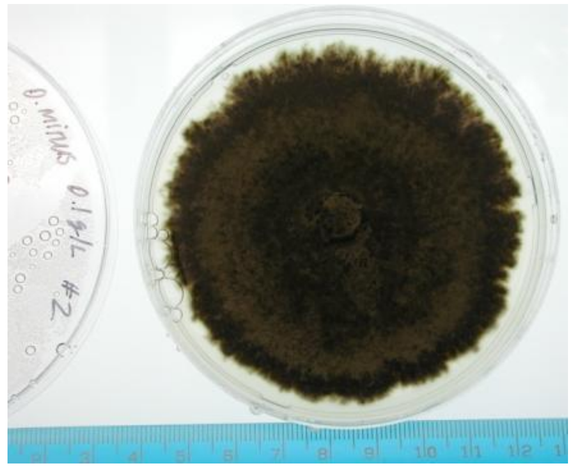
Effects of CCCSNs on Growth of Blue Stain Fungus, *O. Minus*



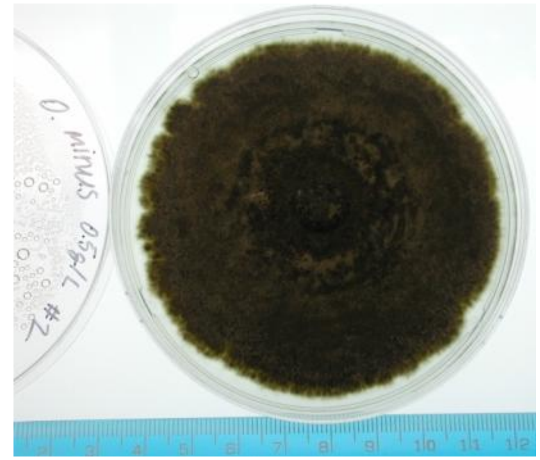
Qi *et al.*, 2011. Potentials of Nanotechnology Application in Forest Protection.

O. MINUS Growth on day 25 Under 6 Concentrations of CCCSNs

Control

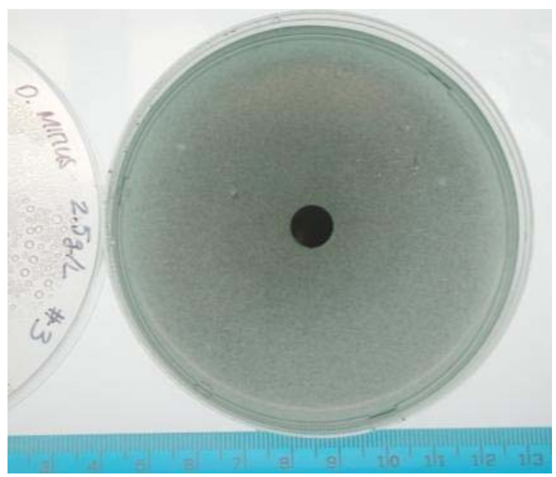


0.1g/l



0.5 g/l

l.0 g/l



2.5 g /l

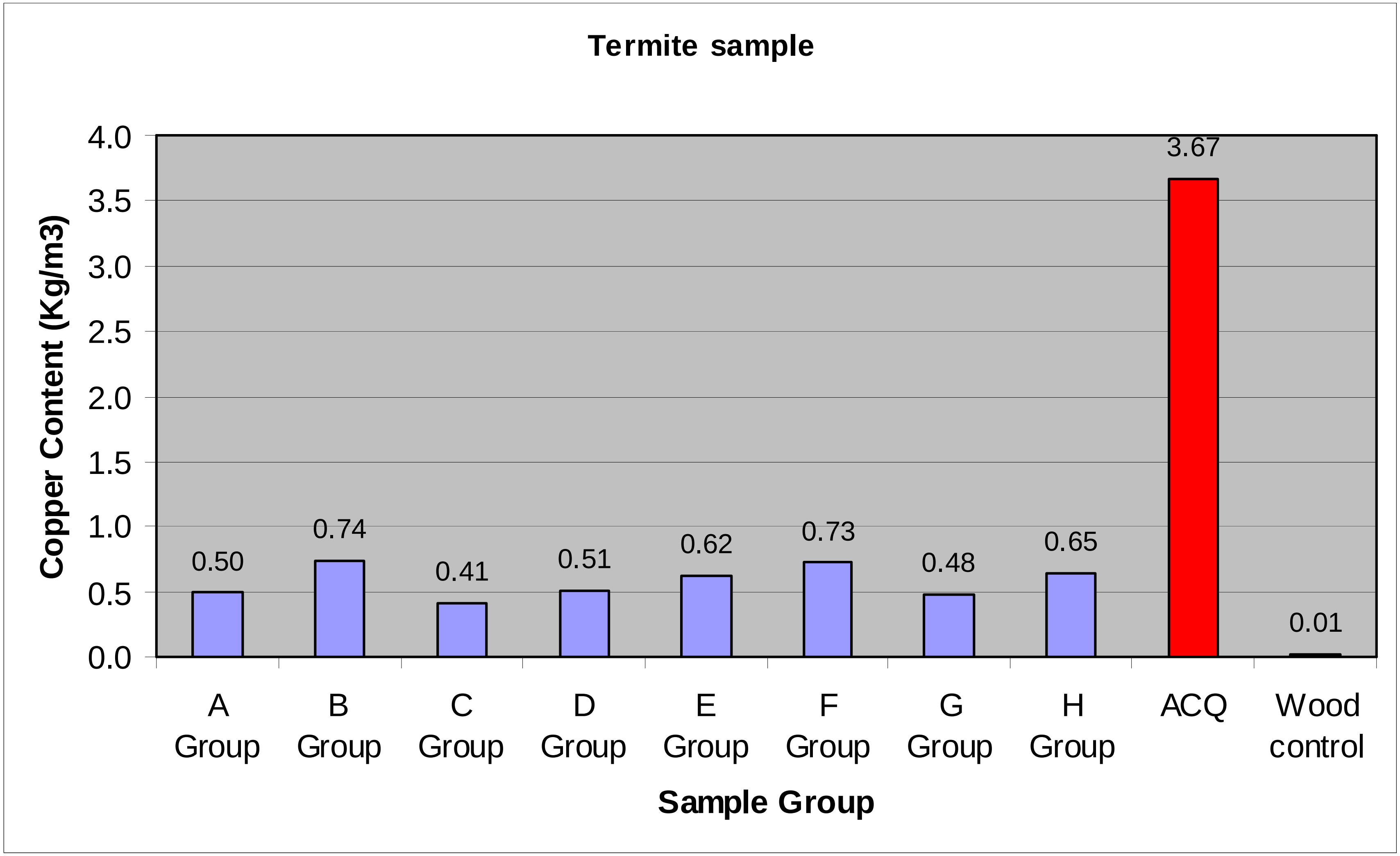
5.0 g/l

Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

Wood Treatment with CCCSNs for Test against Formosa Termite
- Compatible Processing Procedures for Current Manufacture Facilities

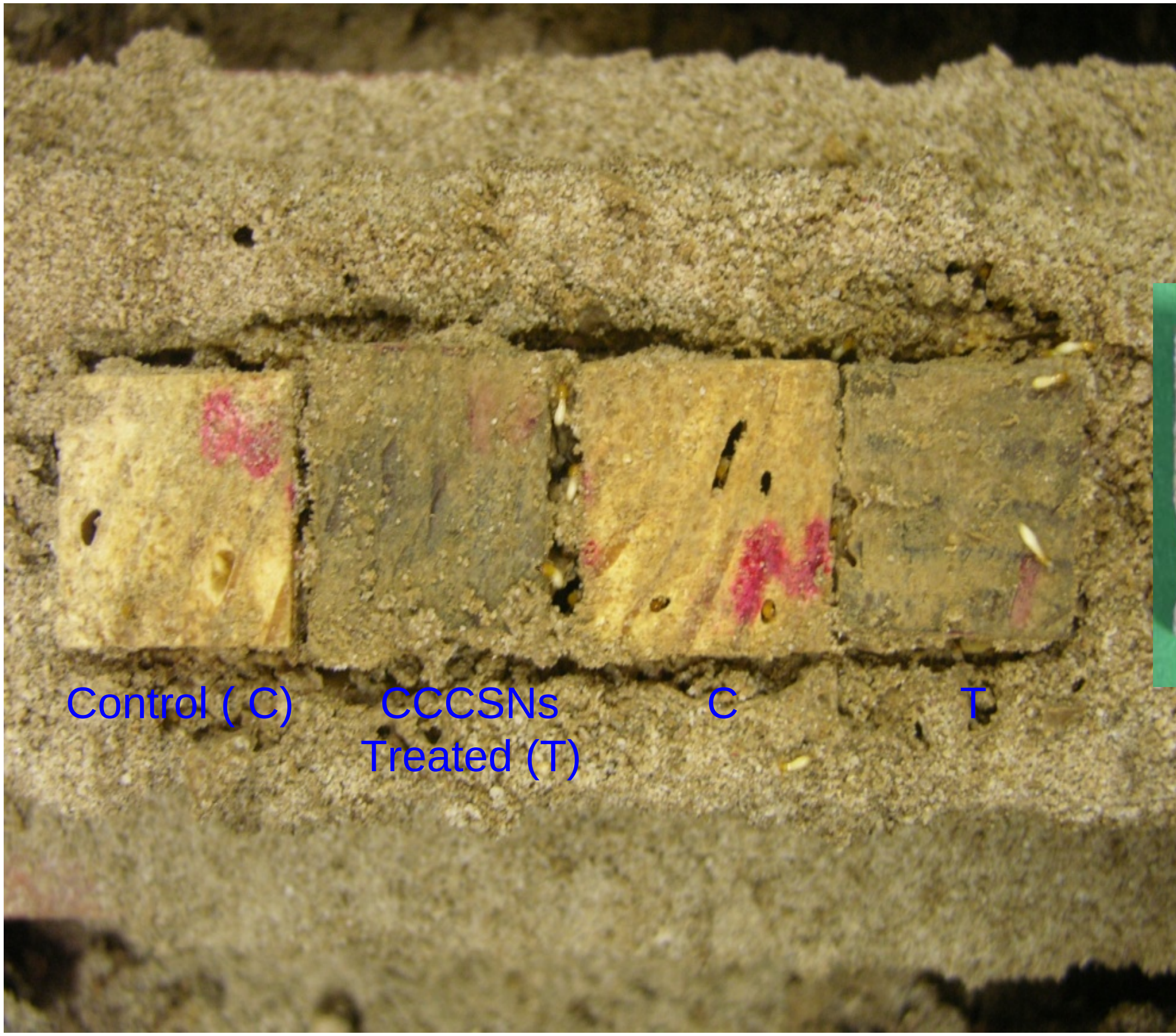
Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

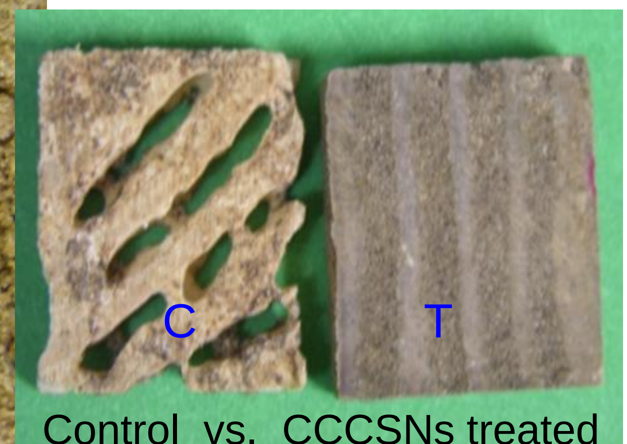
Copper Loading – for Termite Tests



Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

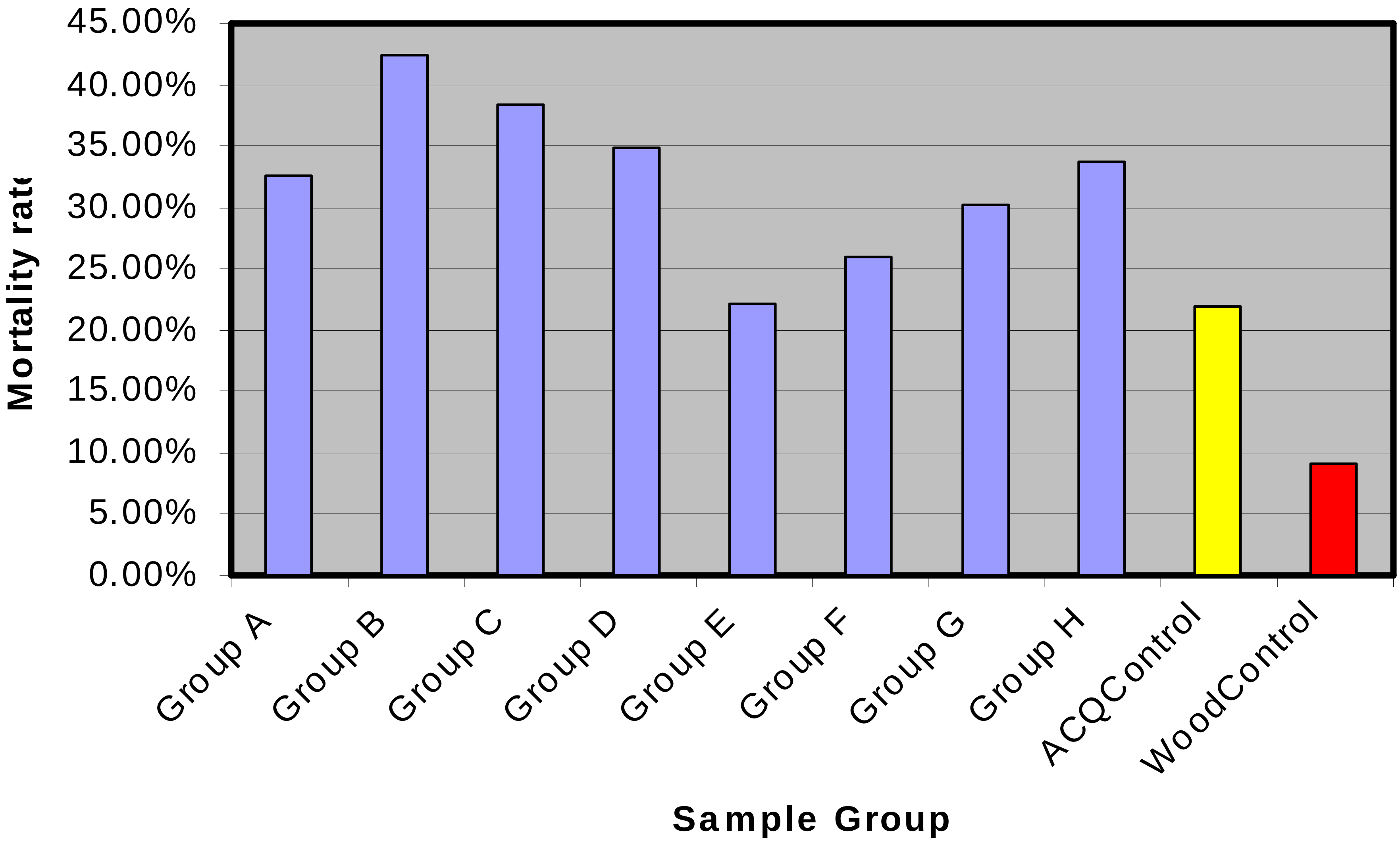
Formosa Termite Test Results





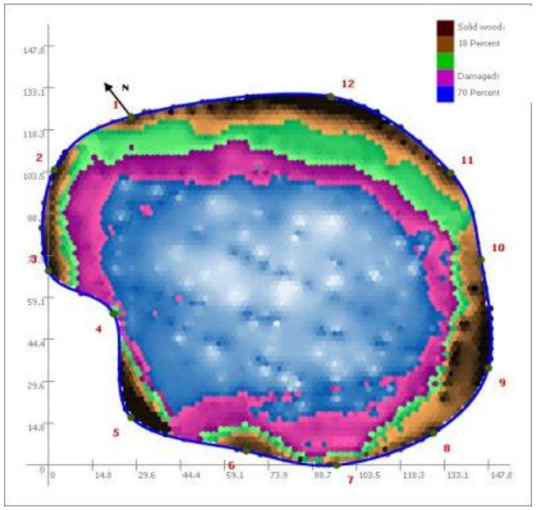
Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

Termite Testing Results (cont.)



Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

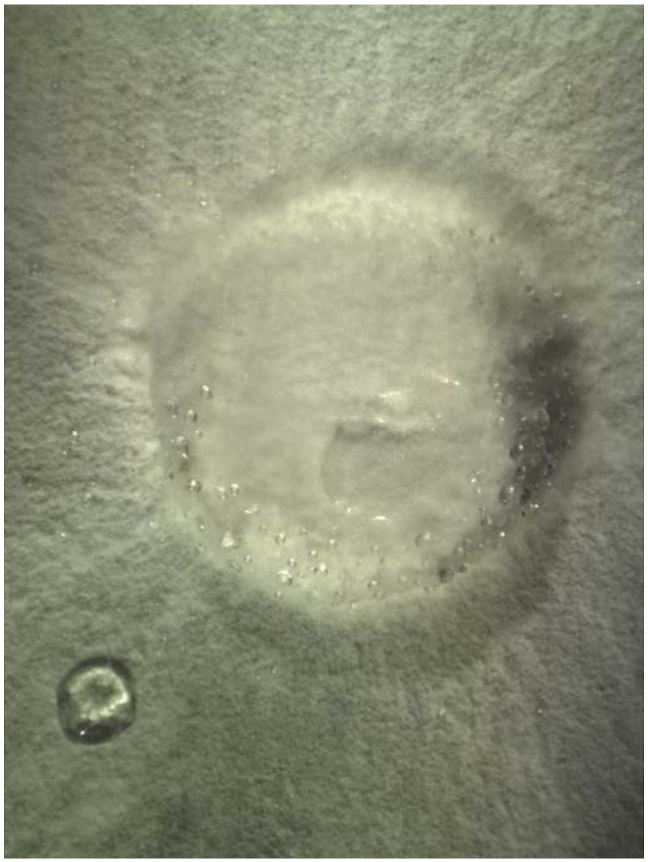
CCCSNs Test against White Rot Fungus

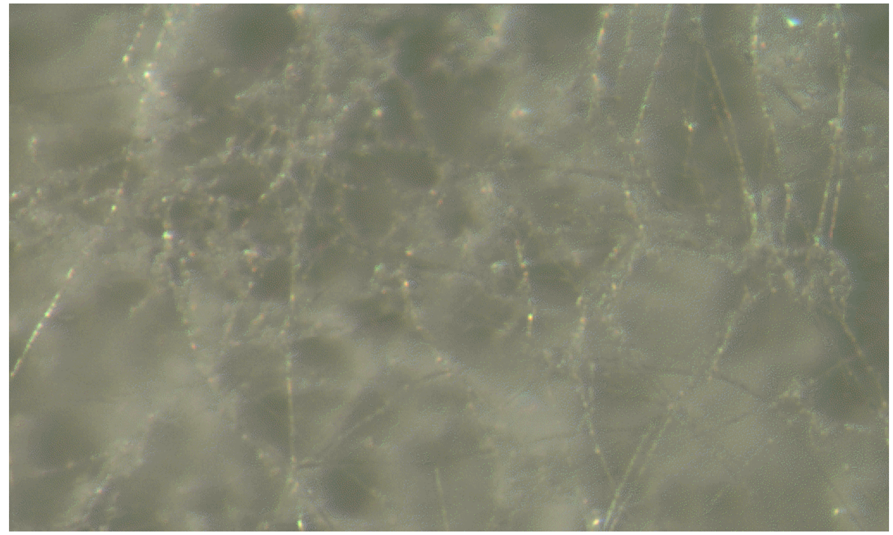


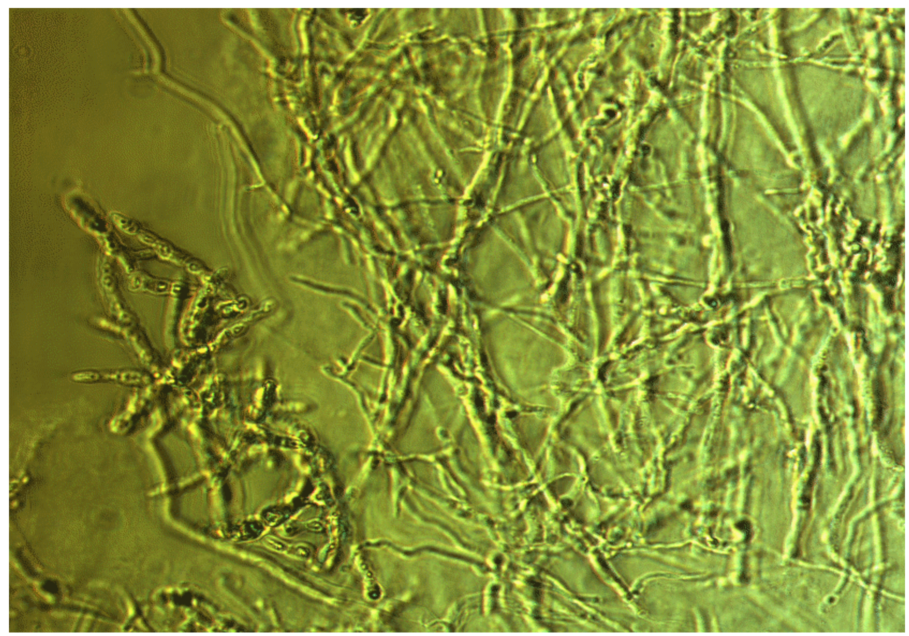
The water oak tree at the right has 70% decay at 15cm above ground, the blue area is hollowed.

Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

Pure Culture of White Rot Decay fungus, *Trametes versicolor*





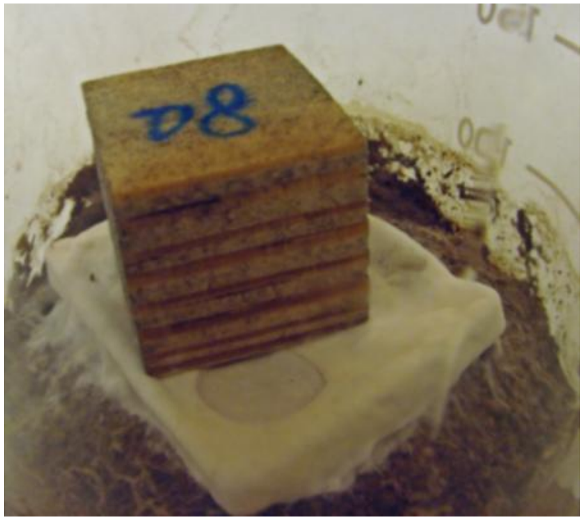


Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

Decay Resistance of CCCSNs Treated Wood against White Rot Fungus, *Trametes versicolor*, -- After 16 Weeks Testing

Control

Treated



Treated

Qi *et al*., 2011. Potentials of Nanotechnology Application in Forest Protection.

Summary

In conclusion, this joint effort will have potential to advance research on Southern pine beetle and other important forest pests, to develop new technologies to protect forest products against woody decay and termites, and to help secure our natural resources and economy.

The project offers a new research field in applied nanotechnology as well as training opportunities for College students in forestry, forest product, and renewable natural resource management.

This research may have broader applications in pest control in the field of Agriculture.

Funding Acknowledgement: USDA-NIFA-CBGP

Thank you

PRESENTED BY

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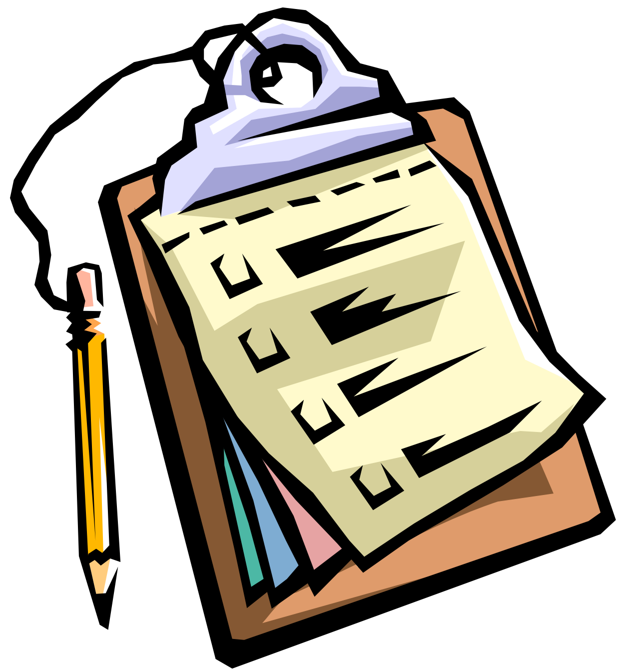

Please remember to turn in your evaluation sheet...