

## Materials and Methods

### Materials

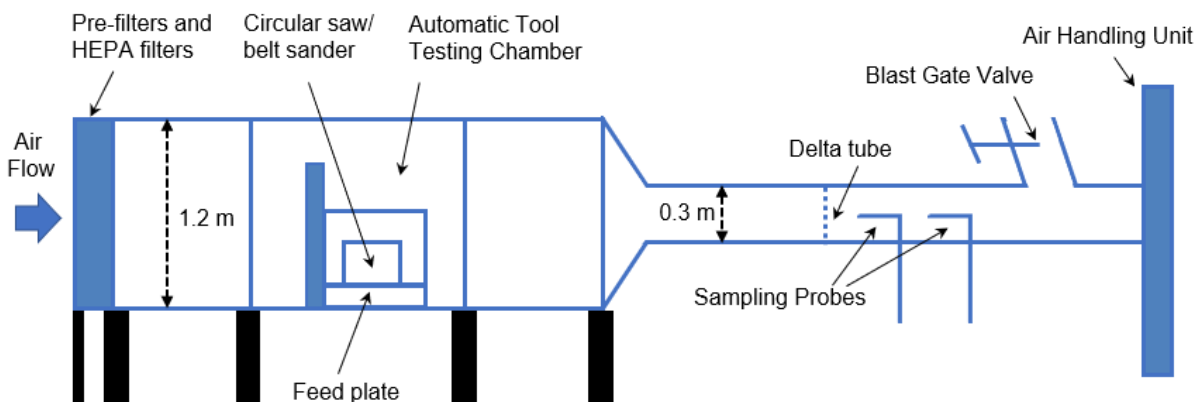
Three types of commercial lumber were purchased from local hardware stores for this study: untreated yellow pine (UYP) and two types of lumber treated with micronized copper azole (MCA) and copper azole type C (CA-C) preservatives, respectively. Both treatments had retention levels for ground contact applications. Specifically, MCA lumber was rated at a retention level of 0.14 pounds of chemicals per cubic foot (PCF, equivalent to 2.2 kg/m<sup>3</sup>) with dispersed copper carbonate and tebuconazole as active ingredients; and CA-C lumber was rated at 0.15 PCF (equal to 2.4 kg/m<sup>3</sup>) containing copper solubilized in ethanolamine and a mixture of tebuconazole and propiconazole as the co-biocides. Reference materials including Cu(II) acetate (powder, 99.99%), Cu(I) oxide (powder, 97%), Cu(II) oxide (powder, <50 nm), Copper(II) carbonate basic (powder, reagent grade) and Cu (powder, 25 nm) were purchased from Sigma Aldrich (St. Louis, MO) for EELS measurements. These materials were used as analogs for Cu compounds that might be present in the samples.

### Thin Section Samples

Thin section samples were prepared by cutting the wood strips cross-sectional and longitudinal using a sliding microtome (Part No. 162-3012, Uchida Yoko, Japan). Then, the uncoated sections were attached to aluminum stubs using double-sided carbon tape to be analyzed by an SEM.

### Aerosol Samples

An automatic laboratory tool-testing system (Fig.1) was used to generate wood dust aerosols during sawing and sanding wood samples. A dust collection and air handling unit (PSKB-1440, ProVent LLC, Harbor Springs, MI) was used as an air mover for the system. The air handling unit was set to draw pre-filtered room air into the testing system at a flow rate of 0.64 m<sup>3</sup>/s (equivalent to 1,350 cubic feet per minute (CFM)). During a sawing test, the system was programmed to run a circular saw (model CS10, Robert Bosch Tool Corp., Mt. Prospect, IL) with a thin-kerf finishing blade having 36 carbide teeth (model DW3176, DeWalt Industrial Tool Co., Towson, MD) and make a preset number of repeated crosscuts at a cutting feed rate of 2.54 cm/s. A brand new saw blade was used for each type of lumber, and the system was thoroughly cleaned between tests of different lumber types to prevent cross-contamination. For the sanding test, a variable-speed belt sander (model 352VS, Porter-Cable, Jackson, TN) was used to sand the surface of a lumber board as the board was advanced along its length using the automatic feeding mechanism. The sander used 240-grit sanding belts (Metalite R228 Abrasive Belt, Aluminum Oxide, Cotton Backing, Norton Saint-Gobain Abrasives, Worcester, MA). Two to three brand new belts were used for each sanding test. A dust cloud generated by each sawing or sanding path was carried downstream by the airflow through the tool-testing chamber and duct before being sampled by various sampling devices. The detailed testing procedures and the diagram of the laboratory testing system can be found in recent studies. In addition, baseline tests were performed when the saw/sander was running but not sawing/sanding any wood to measure the emission from the machines.



**Figure 1.** Diagram of an automatic laboratory tool-testing system for aerosol generation and sampling.

The dust samples were collected on 37-mm diameter, 0.45- $\mu\text{m}$  pore-size Mixed Cellulose Esters (MCE) membrane filters (Part Number 225-9, SKC Inc., Eighty Four, PA) supported by backup pads (Part Number 225-27, SKC Inc., Eighty Four, PA) in three-piece electrically-conductive filter cassettes (Part Number 225-309, SKC Inc., Eighty Four, PA) following NIOSH Method 7402. The sampling flow rate was 12.5 L/min, and a cyclone pre-separator with a  $D_{50}$  of 0.9  $\mu\text{m}$  at this flow rate was used for taking these samples through one of the two sampling probes as shown in Fig 1. The loss for the targeted particles ( $D_{50}$  of 0.9  $\mu\text{m}$ ) in the sampling line was negligible based on calculations. The MCE samples were processed and collected on the 200-mesh nickel TEM grids (Part Number 2620N-XA, Structure Probe Inc., West Chester, PA) using the modified NIOSH Method 7402 for airborne carbon nanotubes and nanofibers.

### Analytical Methods

The surface structures of wood sample sections were examined by using a Phenom XL SEM (Thermo Fisher, Hillsboro, OR) in the low-pressure mode (~60Pa) at 15kV acceleration voltage and 1.7nA probe current with a backscattered electron detector (BSD). The TEM samples were analyzed using a JEOL 2100F TEM (JEOL USA, Peabody, MA) operating at a beam voltage of 200 kV. Bright Field (BF) and High Angle Annular Dark Field (HAADF) images were simultaneously acquired in the STEM mode with a 0.5-1 nm probe size. Elemental analysis was performed at the regions of interest (ROI) with an EDS detector (X-Max80T, Oxford Instruments America, Concord, MA). EELS spectra and energy-filtered TEM (EFTEM) images were obtained using a post-column Gatan Image Filter (GIF) (Tridiem 863, Gatan, Pleasanton, CA). The images and spectra were collected and analyzed with the Digital Micrograph software (Gatan, Pleasanton, CA). Unfiltered and zero-loss (ZL) filtered images were collected to estimate sample thickness variation. Energy-filtered images were acquired in the vicinity of the C-K (284 eV), Cu-L<sub>2,3</sub> (931 eV), and O-K (532 eV) edges using a 25 eV width slit by applying the three-window method. Alignment was applied to correct specimen drift during the acquisition of the pre-edge and post-edge images. After applying a power-law background model, the elemental distributions of C, Cu, and O were obtained from the filtered images. Core-loss energy-loss spectra were recorded at 200 kV using an energy dispersion of 0.2 eV/channel in the STEM mode with the spot size of 1 nm. Zero-loss and low-loss spectra were acquired and later used to calculate the relative thickness of the sample and remove plural scattering by Fourier-ratio deconvolution.