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Sampling and Analysis Study of Treated Wood (Draft)

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Executive Summary

The Department of Toxic Substances Control (DTSC) sampled and analyzed three types of treated wood pursuant to California Code of Regulations (Cal. Code Regs.), Title 22, Section 66262.24. Samples were collected of creosote-treated wood waste (out-of-service railroad ties), Alkaline Copper Quaternary (ACQ-C) treated wood, and Copper Azole (CA-B) treated wood. All railroad tie samples were collected from a railroad maintenance yard in Flanigan, Nevada. This site acts as a collection point for California out-of-service railroad ties. Composite samples were analyzed by DTSC's Environmental Chemistry Laboratory. The sample preparation and analysis protocols were consistent with the requirements of Cal. Code Regs., Title 22, Section 66262.24, and Appendix II of Chapter 11.

The analytical results were compared with California regulatory toxic criteria for hazardous waste. DTSC presents the following conclusions:

1. Wood products treated by ACQ-C and CA-B contain high level of copper, which exceeds California Total Threshold Level of Concentration and Soluble Threshold Level of Concentration regulatory criteria. Therefore, wood products treated by ACQ-C and CA-B have the potential to be a California hazardous waste when disposed.

2. Untreated wood samples were not toxic to fish. The fish survival rate in 500 mg/l dose 96-hour bioassay was 100 percent for all untreated wood samples.

3. Creosote-treated railroad ties contain materials toxic to fish. Sampled out-of-service creosote-treated railroad ties have the potential to fail the California regulated acute aquatic 96-hr LC_{50} bioassay. The survival rates in all three Douglas fir out-of-service railroad tie composite samples were less than 50 percent in 500 mg/l bioassay. Therefore, out-of-service creosote-treated railroad ties have the potential to be a non-RCRA hazardous waste when disposed.

4. Treated wood samples can be prepared by cutting lumber into sections, sub-sections, cubes, and further by grinding to obtain a proportional representative treated and non-treated mixture.

5. Visually distinguishing the treated and non-treated areas at the cross sections of both treated copper-base lumber products and out-of-service railroad ties is feasible.

6. It is the generator's responsibility to determine waste classification.

1. Introduction

Wood is typically treated with chemical preservatives to improve its durability. Arsenic, chromium, copper, pentachlorophenol, and creosote are all used as preservatives in wood. Unfortunately, these chemicals are also known to be toxic or carcinogenic, and certain levels of exposure to these chemicals can pose serious risks to human health and the environment. The Department of Toxic Substances Control (DTSC) has completed a study of chemicals found in treated wood in order to properly manage wood waste. The results of this study show the toxic characteristics of selected copper-based treated wood products and out-of-service creosote-treated railroad ties.

The objectives of DTSC's sampling and analysis study were:

1. To develop a sampling collection plan to obtain representative treated wood material in California;
2. To apply appropriate methods for treated wood sample preparation and analyses; and
3. To determine whether the copper-based and creosote-treated wood exhibit toxicity characteristics that meet regulatory criteria for hazardous waste.

Copper-based preservative treated lumber was sampled from wood products that were treated with Alkaline Copper Quaternary (ACQ-C) and Copper Azole (CA-B) preservatives. The creosote-treated wood was sampled from out-of-service railroad ties. Representative samples were collected from different locations in California by a staff member of University of California Cooperative Extension working as a DTSC contractor. All sample analyses, except aquatic bioassay, were conducted by the DTSC Environmental Chemistry Laboratory (ECL). The aquatic bioassays were performed at a DTSC-contracted laboratory.

The determination of whether treated wood waste is hazardous waste should be conducted in accordance with the California Code of Regulations (Cal. Code Regs.), Title 22, Division 4.5, Chapter 11. It is the generator's responsibility to determine if a waste is a hazardous waste. The generator must determine if the waste exhibits hazardous waste characteristics by testing the waste according to the approved methods or applying knowledge of the hazards characteristic of the waste in light of the processes that the materials have undergone. This study did not try to classify any individual waste stream. Although waste classified as hazardous is generally subject to uniform regulatory management requirements (Cal. Code Regs., Title 22, Chapter 12 through Chapter 20), DTSC developed alternative management standards for treated wood waste (Cal. Code Regs., Title 22, Division 4.5, Chapter 34) that adjusted for the unique circumstances associated with treated wood waste. Treated wood waste that is removed from utility services, or classified as Resource Conservation and Recovery Act (RCRA) hazardous waste, is not eligible for the alternative management standards.

Because treated wood is widely available in California, sampling locations need to be diversified to obtain representative samples. Additionally, because the preservative chemicals are not distributed uniformly inside the treated wood, and the wood is a bulk but grindable (or millable) solid material, it is not easy to obtain a proportional and representative sample from a waste wood stream for laboratory analysis. Field and laboratory preparation of the wood samples becomes important and needs to be specified and standardized. This study demonstrated the sample preparation and analytical methods for millable hazardous solid materials, which are required in Cal. Code Regs., Title 22, §66261.24, and Appendix II of Chapter 11.

2. Background

Many biological organisms, such as insects and decaying fungi, can destroy wood products. The purpose of incorporating preservative chemicals into wood products is to make the wood toxic to organisms that would ordinarily consume it and, thus, to increase its useful service life. The chemical treatment is a surface penetration process, such as pressure treatment. The chemicals are not distributed evenly inside the wood: a higher concentration occurs at the surface, and low or zero levels occur at the center.

There are five categories of preservatives for pressure treatment processes: organo-organometallic; waterborne (acid-based); waterborne (alkali-based); other waterborne; and fire-retardants. In this study, wood treated by Alkaline Copper Quaternary (ACQ-C) and Copper Azole (CA-B) (both alkali-based waterborne), and creosote (an organic preservative) were sampled and analyzed.

At processing facilities, the quality of the treated wood is evaluated by monitoring the penetration and retention of the preservative chemicals in wood and comparing the actual values with those specified in the American Wood Preservers' Association (AWPA) standards [AWPA, 2007]. Retention level refers to the amount of preservative that remains in the wood after the treatment process is complete. It is measured on a weight basis and is typically measured as pounds of preservative per cubic foot of wood (lbs/ft^3) in the assay zone. Standard retention levels required by AWPA vary with the conditions to which the wood is intended to be exposed. Levels are higher when the intended in-service exposure is more severe. For example, wood that is intended to be in contact with soil contains more preservatives than wood to be used above the ground. Required retention levels are also a function of preservative type and the species of wood for a certain product category. For example, for wood used in ground contact in Use Category 4A (UC4A) (see a table in Appendix I), the retention level with ACQ-C treatment is 0.40 lbs/ft^3, but with CA-B treatment, it is 0.21 lbs/ft^3. The minimum retention for creosote-treated coastal Douglas fir in UC4A is 10.0 lbs/ft^3, but for Red Oak, it is 7.0 lbs/ft^3 for commodities less than 5 inches thick, or 6.0 lbs/ft^3 for commodities 5 inches or thicker.

Once treated wood is out-of-service it is considered waste. Wood preserving chemicals, such as arsenic, chromium, copper, pentachlorophenol, and creosote (creosote contains cresol and polycyclic aromatic hydrocarbons) are toxic substances. The waste toxicity characteristics for hazardous waste classification are determined by analyzing the total or leachable/soluble concentrations of the chemicals in the waste and by testing acute LD_{50} and LC_{50}[1] of the waste.

This study did not sample and analyze any wood treated by arsenic/arsenate preservatives because there were numerous data available from early research. Previous research concluded that arsenic in treated wood was hazardous to humans and the environment [Gradient Corporation, 2001 and 2002; US Consumer Product, Safety Commission, 1990]. US EPA excluded arsenic-treated wood waste from RCRA hazardous waste definition, but launched a voluntary consumer awareness program due to the toxicity of arsenic. Since December 31, 2003, the wood treatment industries have been banned from using Chromated Copper Arsenate (CCA) to treat wood for residential uses[2] [US EPA, 2002]. California did not exempt the arsenate-treated wood from the hazardous waste definition.

Besides arsenate preservatives, non-arsenic wood preservatives were developed recently and are available. Among these non-arsenic preservatives, copper is primarily applied with additional co-biocide(s) added to provide additional anti-fungal activity [Laks, 1997]. ACQ-C and CA-B are two commonly used non-arsenic copper-based wood preservatives. Copper is not a US EPA regulated toxic substance, but it is regulated by California as a persistent and bioaccumulative toxic substance. Wastes containing copper exceeding a certain level are regulated as non-RCRA hazardous wastes in California. Thus, it is necessary to measure the total and soluble copper level in the copper-based treated wood waste in order to determine if it needs to be handled as a hazardous waste.

Leaching tests on copper-based preservative treated wood have been conducted by the University of Florida [Townsend, 2003]. Research focused on the comparison of different leaching solutions. Samples were collected from Southern Yellow Pine that was freshly treated by five different preservatives: Alkaline Copper Quaternary (ACQ-D); Copper Boron Azole (CBA-A); Copper Citrate (CC); Chromated Copper Arsenate (CCA-C#1); and Chromated Copper Arsenate (CCA-C#2). Copper was detected in all samples. Because the leaching methods used in this research were different from California's regulatory required leaching method, the leachable copper concentrations could not be compared with California hazardous waste criteria.

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[1] LD_{50} and LC_{50} are toxicological terms. LD_{50} means Lethal Dose, 50% survival; LC_{50} means Lethal Concentration, 50% survival.

[2] CCA had been used for home construction and landscaping.

Creosote and pentachlorophenol (PCP) are the most commonly used organic wood preservatives for treating railroad ties. As a wood preservative, creosote is used alone, or in combination with coal tar or petroleum.

Creosote is a complex mixture of compounds derived from the coking of coal. The composition of creosote varies, depending on the kind of coal, type of coke oven, coking temperature, and time [Leach, 1976]. Creosote is a RCRA listed hazardous waste (U051). Wastewaters, process residuals, preservative drippage, spent formulations (F034), and wastewater bottom sediment sludge (K001) from wood creosote preserving processes are RCRA listed hazardous waste as well. The majority of compounds in creosote are aromatic hydrocarbons (including polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene, acenaphthene, fluorene, and anthracene), alkylated PAHs, benzene, toluene, xylene, and pyridine (65% to 90% of creosote). The PAHs in creosote are toxic to aquatic life [Rotard and Mailahn, 1987; Neff, 1979]. Creosote may also contain cresols (methyl phenols) and other phenols [Wolfgang, 1987] which are regulated by both federal and state law (Code of Federal Regulations [40 CFR], Chapter 1, § 261.24 and Cal. Code Regs., Title 22, Division 4.5, Chapter 11, § 66261.24). US EPA’s risk assessment evaluation led to the identification of creosote as a possible human carcinogen [US EPA, 2003 and 2007]. Therefore, US EPA also terminated use of certain creosote products based on public health, and environmental considerations [US EPA, 2004].

In 1987, the Association of American Railroads (AAR) began a test program to determine if railroad ties would be considered RCRA hazardous waste. A report [Hockensmith, 1994] described six different toxicity leaching testing programs. Among the 39 chemicals in the Toxicity Characteristic (TC) regulatory list, only six were detected at low (near detection limit) concentrations in the extracts: cresol(s); arsenic; barium; lead mercury; and selenium. The analytical results consistently showed that, in general, a railroad tie waste would not be classified as RCRA hazardous waste.

In 2001, a study of hazardous waste classification for railroad ties was conducted at Wheelabrator Shasta Energy Company [DTSC, 2002]. This company uses out-of-service railroad ties to produce bio-fuel. Railroad ties and fly ash samples were collected on site and were analyzed at the DTSC Environmental Chemistry Laboratory (ECL) at Berkeley, California. The analytical results revealed very low metal content in the creosote-treated ties. All tested organic compounds were either non-detectable or at low levels in both leachable and total concentration analyses. This sampling report concluded that railroad tie waste was not hazardous. DTSC’s review of the report identified two points of concern:

1) The sample particle size was not recorded and might not meet the requirements prescribed in Cal. Code Regs., Title 22, Chapter 11, Appendix II subsections (c)(1) and (d)(1). For hazardous waste classification, the millable

solid sample must be milled to pass through a 2 mm (for metals) or 1 mm (for organics) standard sieve before it is analyzed.

2) The detection levels or quantitation limits were set too high for most organic compounds, compared to the regulated threshold levels. For example the regulated Total Threshold Level Concentration (TTLC) of Pentachlorophenol is 17 mg/kg. The analytical result was non-detectable (ND) with a 620 mg/kg quantitation limit, which did not prove that the concentration of pentachlorophenol in the sample was lower than the regulated level.

These two factors make it necessary to reanalyze railroad ties to determine if they have any toxic characteristics of hazardous waste.

The scope of the current study was limited to determine the toxicity of lumber products treated with copper-based preservatives and out-of-service creosote-treated railroad ties. A sampling plan was prepared prior to the sampling activity in order to ensure that representative samples were collected and prepared. In accordance with the test methods given in Cal. Code Regs., Title 22, the total and soluble metals in treated lumbers and semi-volatile organic compounds in creosote ties were analyzed. All samples were tested for their acute aquatic 96-hour LC_{50} (see page 3, footnote 1). The toxicity characteristic determination was based on California regulatory toxicity criteria (Cal. Code Regs., Title 22, §66261.24).

3. Field Sample Preparation

The total samples used for each composite sample are listed in Table 1.

Table 1 Number of Samples and Sources of Each Composite Sample

Preservatives	Wood Species	Number of Samples	Number of Collecting Location Points	Number of Replicates (Composite Samples)	Name of Composite Samples (Collector's No.)
CA-B	Douglas fir	80	5	4	CADF-COMP
	Hem-fir Species Group (white fir)	80	4	4	CAHF-COMP
ACQ-C	Douglas fir	80	11	4	ACQDF
Creosote	Douglas fir	62	1	3	DF creosote Comp
	White Oak	18	1	1	HW (oak) creosote
Untreated	Douglas fir	80	10	4	DFCONTROL-COMP
	Hem-fir Species Group (white fir)	20	1	1	HFCONTROL-COMP
	White Oak	20	1	1	Oak control

Representative treated wood samples were collected. In order to obtain general characteristics, at least 18 individual lumber/railroad tie samples with the same preservative and same wood species were collected and combined to form one composite sample for analysis[3]. Replicated samples were collected simultaneously. Untreated wood samples were collected in the same manner for quality control purpose.

3.1 Sampling Locations

Copper-based preservative treated lumber samples were collected from Home Depot stores and lumber yards statewide. Two species of woods were selected: white fir (Hem-fir species group) and Douglas fir, which are both softwoods (gymnosperms). As per DTSC's sampling plan, the copper-based preservative treated lumber samples included two CA-B treated wood species and one ACQ-C treated wood species. The UC4A standard retention level for ACQ-C is 0.4 lb/ft^3, and for CA-B is 0.21 lb/ft^3 (see Appendix I).

Sampling locations are listed in Tables 1 – 4 in Appendix II. Tables 1 and 2 list the source locations for CA-B and ACQ-C treated Douglas fir samples, respectively. Table 3 shows the source locations for CA-B treated Hem-fir. ACQ-C treated Hem-fir samples were not collected. Table 4 shows the source location of creosote treated railroad ties.

Even though the wood might have been treated by different companies, the copper-based preservative chemicals were obtained from the same manufacturers and were applied using the same standards provided by the AWPA. The CA-B preservative was produced by Arch Wood Protection, Inc., and the ACQ-C preservative was produced by Osmose, Inc.

With the collaboration of the industry, all creosote-treated railroad tie samples were obtained from the Union Pacific Railroad Company at a collection yard operated by RTI Railroad Services, Flanigan, Nevada. Union Pacific Railroad is the largest railroad company in North America. The railroad ties at this yard are considered to be representative of railroad ties that are out-of-service. Treated railroad tie samples were collected from two species of wood as well: white oak (hardwood species group) and Douglas fir.

Three untreated wood control samples were selected and obtained from different locations. Untreated Douglas fir lumber was purchased at various lumber yards. Untreated white fir (Hem-fir species group) lumber was obtained at a Mendocino Forest Products lumber mill in Ukiah. Untreated oak was obtained from one-inch boards

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[3] The use of composite samples in this study was to obtain statewide general data on treated wood toxic characteristics, not to classify any single waste stream. Composite sampling is not appropriate for individual generator's waste classification purposes.

purchased from a lumber yard in Berkeley. This yard carries oak from many locations, primarily from the Midwestern United States.

3.2 Field Preparations

The lumber or railroad ties were first sawn into sections, then cut into quarters or cubes in the field prior to delivery to the ECL laboratory. Different cutting processes were used to break down the lumber treated with the copper-based preservatives and the creosote-treated railroad ties. The intent in each case was to provide a proportional mixture of treated and untreated material for analysis. The control samples were sawn following the same process as the treated wood samples. The field sample preparations for wood lumber and railroad ties are described in detail in the following sections.

3.2.1 Field Preparation of Copper-based Treated Lumber

Three sample allocations were identified in each 8-ft CA-B and ACQ-C treated lumber product (nominal 2”x 8”x 8’). These samples were designated ‘left’, ’center’, and ‘right’, respectively, and were allocated at 2, 4, or 6 feet from one end of the lumber. A 0.25-inch section was cut from one randomly selected location. This section was used in the laboratory analysis. The remaining portion of each 8-ft lumber was retained so that additional sections can be processed if necessary. Figure 1 in Appendix III shows photographs of the breakdown process. Tables 5-8 in Appendix II list the selected sample allocations. The sample sections were further divided into quarters and were stored in glass jars, which were sealed to ship to ECL. Quarter-sections were prepared to facilitate further processing at ECL. Figure 2 in Appendix III shows the quarter cutting and storing process. From the cross section pictures, the treated and untreated portions of the lumber can be identified.

For each selected treatment-species combination, four replicate samples were collected and processed simultaneously. The replicated sections were separately stored in four boxes prior to further quartering. Each replicate would be composed as one final sample in the laboratory (Figure 3 in Appendix III).

A chop (cross cut) saw was used to process the lumber into sections. A new blade was used to process samples from woods treated with different preservatives. Alcohol in a spray bottle was used to clean the blade in between processing samples.

A band saw was used to process the 0.25-inch sections into quarter sections. A new band-saw blade was used for each replication.

As copper is not a toxic contaminant under federal hazardous waste regulations, there was no need to prepare the cubes for the leaching test.

3.2.2 Field Preparation of Railroad Ties

The sampled out-of-service railroad ties, randomly selected from out-of-service tie bundles, were shipped to the yard in open-top train containers. Douglas fir and white oak ties were sampled separately. To protect the chain saw, metal spikes and other contaminants were removed before cutting. Two cross-cut sections, two to three inches thick, were cut from individual ties using a chain saw. One of the sections was randomly selected as the sample for laboratory analyses. The railroad tie sample selection is shown in Table 4 of Appendix II. A total of 80 railroad ties were cut: 62 treated Douglas fir railroad ties formed three composite samples, and 18 treated oak railroad ties formed one composite sample.

Collecting a cross-cut section from railroad ties was difficult. The original sampling plan specified four replicate samples for analysis. A total of 80 samples would be required to form four composites with 20 samples each. However, the removal of metal spikes and other miscellaneous metal contaminants in the railroad ties damaged the railroad ties, and it was difficult to obtain more than two complete cross-cut sections from an out-of-service railroad tie.

The cross-cut sections were laid flat and wrapped with aluminum film prior to further processing. Two sub-sections (0.9 cm x 0.9 cm x random length) were cut from the cross-cut section at visually determined representative areas. The size and locations of sub-sections varied depending on the various shapes of the cross-cut sections. Some cross-cut sections got split into pieces after cutting due to weathering damage or metal spike removal. Figures 4 and 5 in Appendix III are examples of the cutting. The treated and untreated areas could be visually distinguished. For two types of laboratory analysis, one sub-section was further cut into 0.9 cm cubes at field, and another sub-section was prepared for further processing (grinding) at ECL. All cubes and sub-sections were stored in glass jars.

A chain saw was used to cut the cross-cut sections. A chop saw was used to expose a fresh surface and to prepare sections for band sawing. A band saw was used to cut the grinding sub-sections and 0.9 cm cubes. Alcohol from a spray bottle was used for decontaminating the chop saw and band saw blades in between processing samples.

Note that the three railroad tie Douglas fir composite samples were not replicate samples. The creosote-treated samples were collected from different railroad ties at random allocations along the length. Samples were individually collected, then composited in the laboratory.

3.2.3 Field Preparation of Control Samples

All untreated Douglas fir samples were cut at two feet from the end piece of lumber. For each wood species, twenty sections were cut, except Douglas fir. Eighty samples were collected for the Douglas fir. The extra amount of untreated wood was used for cleaning the laboratory mill. For metal analysis and bioassays, four composite samples were used, but combined as one composite sample for organic analysis. Some quarters were cut into 0.9 cm cubes and stored in a jar for a leaching test. The remaining quarters were put in jars for grinding.

4. Analytical Procedures

4.1 Particle Size Reduction

All sampled quarters/sub-sections of lumber and ties were ground to pass through a No. 10 (2 mm) standard sieve before they were analyzed, except the 0.9 cm railroad tie cubes that would be extracted by the Toxicity Characteristic Leaching Procedure (TCLP). Figure 6 in Appendix III shows a Thomas-Wiley Laboratory Mill, Model 4 that was used for this project. The mill has a 2 mm sieve at the outlet. The composite samples were milled in this order: DFCONTROL-COMP; CADF-COMP; ACQDF; CAHF-COMP; HFCONTROL-COMP; DF Creosote Comp; HW (oak) Creosote; and Oak Control (see Table 1 in Section 3 for sample names). Before and after grinding each composite replicate, the mill was cleaned using brushes, laboratory spatulas, and compressed air. Once clean of particulate matter, the mill was wiped with acetone. To avoid any analyte carry-over between replicates, approximately 50g of untreated Douglas fir was milled, and then discarded.

4.2 Composite Samples

The milled wood was mixed in an aluminum pan using a plastic scoop until homogeneous (evidenced by a uniform color distribution). About one-half of each composite sample was transferred to pre-cleaned sample jars that were distributed for the analyses. The remaining samples were retained in sealed polyethylene bags.

Portions of the four untreated Douglas fir samples were further composited as one sample (DFCONTROL-COMP) for organic analyses.

Cube samples that did not need to be ground were simply mixed as per analytical requirements.

4.3 Sample Analyses

4.3.1 Metal Analyses

Metal contents were analyzed by the ECL Berkeley Inorganic Section. Only the copper-based preservative treated wood and untreated control wood needed to be tested for metal content. All metals listed in Cal. Code Regs., Title 22, § 66261.24 (a)(2)(A) were analyzed for both total and extractable concentrations, which were compared to their Total Threshold Limit Concentrations (TTLC) and Soluble Threshold Limit Concentrations (STLC), respectively.

The wood samples were acid-digested using US EPA Method 3050B and analyzed using Method 6010B, Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) for total metal concentration. The extractable metal concentration was determined using California Waste Extraction Test (WET) and Method 6010B.

4.3.2 Organic Compound Analyses

Railroad tie samples were tested for organic compounds. Cal. Code Regs., Title 22 § 66261.24 (a)(1) and (a)(2)(B) list Toxicity Characteristic (TC), TTLC and STLC, respectively. This study did not analyze the organic soluble concentration using WET because the total concentrations were very low.

The TCLP is a procedure to determine a leachable concentration. Approximately 100 grams of cubed creosote-treated or untreated Douglas fir or white oak samples were extracted with two liters TCLP extraction fluid #1 (20:1 ratio), which is an acetate buffer at pH 4.93 ±0.05. The cube sample and extraction fluid were put into PTFE bottles, which were then put into a TCLP rotary agitation device (Associated Design and Manufacturing, Alexandria, VA). After 18 hours, the samples were filtered using a pressure filtration device (Millipore, Inc., Bedford, MA) and GF/F filters. Figure 7 in Appendix III shows the devices. The filtrates (light brown for the controls, and dark amber for the creosote samples) were transferred to labeled bottles, and then sent, packed in ice, by overnight courier to ECL at Los Angeles for analysis.

The aqueous TCLP extracts were solvent-extracted within the seven-day holding time specified by the TCLP (SW-846, Method 1311).

The total semi-organic (SVOC) concentration was obtained from the milled railroad tie samples. The milled wood samples were extracted by Method 3540, Soxhlet extraction. The wood extracts were then subjected to a gel permeation column cleanup, Method 3640, to remove interferences.

Both cubed and milled wood extracts were analyzed by gas chromatography with a mass selective detector (GC/MS), with US EPA Method 8270C. The cube sample results were compared with TC, and the milled sample results compared with TTLC. The analyses in this project did not limit the regulated organic compounds, but also quantified, if possible, all compounds on the Method 8270 target list.[4]

4.3.3 Aquatic Bioassay

Aquatic bioassays were conducted at Associated Laboratories in Orange County, California using *Pimephales promelas* (fathead minnows) as the test organism. In accordance with California Department of Fish and Game procedure, the milled wood sample was shaken for 6 hours with water (50 g: 50 ml) to disperse the sample before an aliquot was taken and added to the aquarium water. Aliquots of this mixture were then added to the aquarium. The bioassays conducted in this project were screening procedures. The wood concentrations were added at three doses: 250 mg/l; 750 mg/l; and 500 mg/l. The 500 mg/l dose was run in duplicate. The results were compared with the California acute aquatic 96-hr LC_{50} toxicity characteristic level.

5. Quality Control and Quality Assurance

As mentioned above, untreated wood samples were collected and analyzed simultaneously as background control samples. The purpose was to assure that the wood matrix itself was not contaminated by chemicals or harmful to aquatic life.

In order to assure that the mill process does not cause any cross contamination, after each composite sample was ground, and 50g untreated Douglas fir was ground and discarded, another 50g Douglas fir was ground and retained as a mill blank (MB). One MB was prepared before the first sample and after each treatment replicate.

Standard methods established in U.S. EPA publication SW-846 and ECL quality control procedures were followed for the metals and organic analyses. Method blanks, solid laboratory control samples (LCS), method standards, matrix spikes (MS), and matrix spike duplicates (MSD) were analyzed.

Triplicate extractions and analyses were conducted on the copper-based treated wood composites. Matrix spikes for the soluble metal concentrations were done after extraction and dilution, and before instrumental analyses. Daily multi-point ICP-AES calibration standards and a reagent blank were run to establish response linearity, and calibration verification standards were analyzed after every ten samples.

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[4] It would be valuable to determine if any other kinds of organic compounds, such as PAHs, were present in creosote-treated wood or their TCLP leachates. Some organic compounds may be interesting as environmental contaminants, but may not have regulatory TC and TTLC levels.

For the solvent extraction and GC/MS analysis, standard ECL and SW-846 quality control practices were followed. Method blanks, method standards, surrogates, matrix spikes, and matrix spike duplicates were analyzed to assess bias (accuracy) and precision. For quantitation, multi-point calibrations were conducted using commercially available reference mixtures. Response factors were verified by analyzing continuing calibration check standards. Analyte identification was performed by comparison of the unknown and reference compound spectra, using characteristic ions.

For the aquatic bioassay, the contract laboratory used three sample dilutions; each dilution was run in duplicate. A control was run for each batch using un-spiked waste.

6. Results and Discussion

All analytical results were summarized in Table 2. The concentrations shown in this table are average values of replicate sample results if there was more than one replicate. The total cresol concentrations in this table were the sum of concentration of 2-methylphenol and 4- and/or 3-methylphenol.

Discussions about the analytical results on metal, semi-volatile organic compounds, and acute aquatic LC_{50} are presented below. Tables 3-6 show these analytical results in more detail than Table 2, respectively.

All laboratory analytical data are reported in Appendix IV. Since samples CADF-COMP, CAHF-COMP, ACQDF, DF creosote Comp have replicate composite samples, the names of the samples are CADF-COMP1, CADF-COMP2. MB indicates mill blank or equipment blank (see Section 5 above).

Most metals were non-detectable (ND) in the copper-based preservative treated lumber samples, except barium, copper, and zinc. Trace levels of barium and zinc were found in both treated and untreated control samples.

Copper concentrations exceeded regulatory threshold levels (TTLC and STLC) in all samples, except three CADF composites. However, the average copper concentration in four CADF composite samples was higher than its TTLC (2,500 mg/kg) (see Table 3). Therefore, the copper-based treated lumber products, when disposed, should be handled as a non-RCRA hazardous waste.

Table 2

Comparison of Analytical Results with California Waste Classification Criteria

Name of Composite Sample	Number of Replicates Averaged	Metal Total Concentration vs. TTLC	Metal Soluble Concentration vs. STLC	Organic Total Concentration vs. TTLC	Organic Leachable Concentration vs. TC	96-hr Aquatic Bioassay LC_{50} Results *	Hazardous Waste when disposed **?**
CADF-COMP	4	**Only Cu exceeded 2518 vs. 2500 mg/kg**	**Only Cu exceeded 218 vs. 25 mg/l**	N/A	N/A	Not less	**Yes**
CAHF-COMP	4	**Only Cu exceeded 4843 vs. 2500 mg/kg**	**Only Cu exceeded 468 vs. 25 mg/l**	N/A	N/A	**<250 mg/l**	**Yes**
ACQDF COMP	4	**Only Cu exceeded 3900 vs. 2500 mg/kg**	**Only Cu exceeded 365 vs. 25 mg/l**	N/A	N/A	Not less	**Yes**
DF Creosote Comp	3	N/A	N/A	ND **	ND***, except trace Total Cresol 1.4 vs. 200 mg/l	**<250 mg/l**	**Yes**
HW (oak) Creosote	1	N/A	N/A	ND **	ND***, except trace Total Cresol 0.42 vs. 200 mg/l	Not less	No
DFCONTROL-COMP	4	ND	ND	ND	ND	Not less	No
HFCONTROL-COMP	1	ND	ND	ND	ND	Not less	No
Oak Control	1	N/A	N/A	ND	ND	Not less	No

ND -- non-detectable N/A -- not analyzed

* The regulated 96-hr acute aquatic LC_{50} is less than 500 mg/l.

** Some organic compounds that have no regulatory TTLC were detected: naphthalene, acenapthalene, acenapthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, ideno(1,2,3-cd)pyrene, benzo(ghi)perylene, phenol, 2,4-dimethyl phenol, carbazole, 2-methyl naphthalene, dibenzofuran, and 4-nitroanaline.

*** Some organic compounds that have no regulatory TC were detected: naphthalene, acenapthalene, acenapthene, fluorene, phenanthrene, phenol, 2,4-dimethyl phenol, carbazole, and dibenzofuran.

Table 3 Copper Concentrations in Samples

Sample	Total Copper Concentration (mg/kg)					Soluble Copper Concentration (mg/l)				
	COMP 1	COMP 2	COMP 3	COMP 4	*AVERAGE*	COMP 1	COMP 2	COMP 3	COMP 4	*AVERAGE*
CADF-COMP	2480	2420	2730	2440	**2518**	213	198	245	216	**218**
CAHF-COMP	4890	4680	4630	5170	**4843**	447	457	452	515	**468**
ACQDF COMP	3980	3790	3860	3970	**3900**	364	356	360	378	**365**
DFCONTROL -COMP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
HFCONTROL -COMP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Because this study was not done on out-of-service lumber samples, it is hard to predict how much copper was left in the treated lumber after service. The copper levels in out-of-service treated lumber may vary in a range, depending on their service condition (above ground, under ground, soil or water contact, and weather conditions) and service age. However, as the level of copper in the lumber products was at such a high level, compared with the regulatory threshold level, the out-of-service copper-based preservative treated lumber may exhibit a toxicity characteristic as well.

The CADF samples contained much lower copper concentration than ACQDF samples, and the CA-B treated Hem-fir special group (white fir) sample contained the highest copper concentration, which may be due to originally different retention levels for different combinations of wood species and preservatives.

Many semi-volatile organic compounds (SVOCs) can be analyzed by GC/MS (US EPA SW-846, method 8270C). However, only a few of them have their regulatory TTLC and TC. Most regulated SVOCs in the out-of-service creosote railroad tie samples are non-detectable (ND), except very low levels of cresol (methyl phenol). The leachable cresol concentrations ranged from ND to 0.94 mg/l, much less than its TC 200 mg/l. The total cresol concentrations ranged from 10 to 100 mg/kg, but there is no TTLC level for cresol. Please see Table 4 for the cresol concentrations in samples.

Both leachable (using TCLP) and total concentrations of pentachlorophenol (PCP), which are regulated, in all railroad tie samples were reported ND. The total concentrations of PCP were reanalyzed since the first analysis reported the PCP quantitation limit at 25 mg/kg or 50 mg/kg. In order to compare with the PCP regulatory TTLC (17 mg/kg), the second analysis reported ND again with a PCP quantitation limit of 10 mg/kg.

Table 4 Total and Leachable Semi-Volatile Organic Compounds (SVOC) in Creosote-Treated Railroad Ties

Sample	Total SVOC (mg/kg)					Leachable SVOC (using TCLP) (mg/l)				
	Cresol	PCP	Total PAHs*	Phenolics**	Hetero-cycles***	Cresol	PCP	Total PAHs*	Phenolics**	Hetero-cycles***
DF Creosote Comp1	69	<10	11,830	103	750	1.40	<0.5	3.3	2.54	0.30
DF Creosote Comp2	120	<10	19,328	246	1,700	<0.04	<0.5	4.5 & 3.5	<0.04	<0.04
DF Creosote Comp3	130	<10	16,838	275	1,500	<0.04	<0.5	4.7 & 3.9	<0.04	<0.04
HW (Oak) Creosote	43	<10	8,148	43	680	<0.04	<0.5	3.1	0.71	0.34
DFCONTROL-COMP	<2	<10	<2****	<2****	<2	<0.04	<0.5	<0.04	<0.04	<0.04
Oak Control	<2	<10	<2****	<2****	<2	<0.04	<0.5	<0.04	<0.04	<0.04

* The PAHs include napthalene, acenapthene, acenapthalene, fluorene, phenanthrene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, ideno(1,2,3-cd)pyrene, benzo(g,h,i)perylene, and 2-methyl naphthalene.

** The phenolics include phenol, 2,4 dimethyl phenol, 2-methylphenol, and 4-&/or3-methylphenol.

*** The hetero-cycles include carbazole and dibenzofuran.

**** The Quantitation Limit of total concentration for naphthalene, acenapthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, carbazole, 2-methyl naphthalene, and dibenzofuran for some samples is 200 mg/kg, for 2,4 dinitrophenol, 2-methyl-4,6-dinitrophenol, and 4-nitro phenol is 25 mg/kg.

Some organic compounds that are not listed in TTLC and TC regulated tables were detected, including polycyclic aromatic hydrocarbons (PAHs) that are toxic. Table 4 also shows the other regulated and non-regulated SVOCs in the creosote-treated railroad tie samples. DTSC summarized the total PAHs, phenolics, and hetero-cycles that were found in the creosote-treated railroad tie samples in Table 4.

Table 5 Total vs. Leachable (using TCLP) Concentrations of PAHs

PAH	naphthalene	acenapthene	fluorene	phenanthrene
Total (mg/kg mean, n=4)	2400	1600	675	3100
Leachable (mg/l mean, n=6)	3.2	0.27	0.13	0.18

Compared with their total concentrations, the leachable concentrations were much lower than expected. Table 5 lists a few PAHs average total and leachable concentrations. These results reveal that the PAHs in creosote-treated wood were not highly leachable.

Only two kinds of composite samples could not pass the 96-hour aquatic bioassay LC_{50} regulatory level (500 mg/l) (see Table 6). One was CA-B treated Hem-fir (white fir). It also contained more copper than the other two copper treated lumbers – ACQ-C treated Douglas fir and CA-B treated Hem-fir (white fir). The other was out-of-service creosote-treated Douglas fir. Three replicate samples all had an LC_{50} less than 250 mg/l. The results indicate that the sampled creosote-treated Douglas fir waste could be a potential non-RCRA hazardous waste. Different from the Douglas fir railroad tie samples, the creosote-treated Oak ties did not fail the aquatic bioassay analysis, although the survival rates were 60 and 70 percent for the duplicate bioassays at 500 mg/l. The fish survival rate in all 500 mg/l untreated wood bioassay tests was 100 percent, which indicated that the untreated wood is not toxic to fish.

Table 6 Results of Acute Aquatic 96-hr LC_{50} Tests

Sample	LC_{50} (mg/l)	Survival Percentage (500 mg/l)
CADF-COMP (n = 4)	>750	100%
CAHF-COMP (n = 4)	<250	0%
ACQDF COMP (n = 4)	>750	100%
DF Creosote Comp1	<250	20% & 10%
DF Creosote Comp2	<250	20% & 10%
DF Creosote Comp3	<250	10% & 0%
HW (oak) Creosote	>500	60% & 70%
DFCONTROL-COMP (n = 4)	>750	100%
HFCONTROL-COMP	>750	100%
Oak Control	>750	100%

The aquatic bioassay results on railroad ties are different from those previously obtained by Wheelabrator Shasta Energy Company. The difference could be caused by the wood species, the particle size, or the age of the railroad ties. The bioassay results obtained in this study reflect that certain railroad ties are hazardous to fish. Although the aquatic bioassay in this study was a screening test, the results indicate that it is necessary to take into account bioassay results prior to discharging the railroad tie waste.

Although staff of DTSC and University of California Cooperative Extension carefully planned this sampling study, many uncertainties still exist. For example, the wood moisture was unknown, which may affect the results. The service years of creosote-treated ties were undetermined, and could be a significant range.

Additionally, uncertainties arise from the practical realities of sample collection. Selected sampling locations must be representative of California. DTSC initially planned to collect samples from approximately 20 locations statewide. However, DTSC found that most lumber yards carry only one kind of treated lumber, so it is rare to find all three treated wood species at one lumber yard. Thus, the samples were collected from fewer locations than planned.

Notwithstanding these uncertainties, DTSC believes that the composite samples are representative of California's treated wood. The high levels of copper in the treated wood with copper-based preservatives are significant.

There are different sizes of lumber and timber available in the California market. Because the wood treatment is a surface process, it is reasonable to assume that the higher the ratio of surface to volume, the higher the concentration of preservative is absorbed. The 8”x 8” lumber, which DTSC did not sample, may have less copper concentration than the 2”x 8” lumber. The surface to volume ratio for a large timber is smaller. The surface to volume ratio for an 8” x 8” is 0.52, and for a 4” x 4” is 1.02. The 2” x 8” lumber was selected because it is fairly common, and its surface area to volume ratio is approximately 1.27. This study did not plan to collect other sizes of lumber.

This project studied the commonly commercially available wood treated by copper-based wood preservative. It was not DTSC’s intent to compare the different chemical manufacturers. Therefore, DTSC did not research different chemical companies’ products during the sampling.

In accordance with Cal. Code Regs., Title 22, Chapter 11, Appendix II, two millimeter (2 mm) or less of particle size is required for: (1) total and extractable metal content listed in Section 66261.24(a)(2)(A); and (2) extractable organic content listed in Section 66261.24(a)(2)(B) if the waste is a millable solid. One millimeter (1 mm) or less of particle size is required for total content of organic listed in 66261.24(a)(2)(B) if the waste is a millable solid. The US EPA sample extraction Method 3540 for semi-volatile organic compounds in solid sample (by Soxhlet extraction) also calls for 1 mm particle size.

The composite samples prepared in ECL were all milled to pass through the 2 mm sieve. Further grinding would have caused excess heat in the mill that may have degraded the sample. For fibrous samples, Method 3540 states that particle size reduction should be sufficient to ensure contact with solvent. Appendix III in Cal. Code Regs., Title 22, Chapter 11, states that SW-846 should be consulted for appropriate methods for each “specific sample analysis situation.” It was therefore determined that the 2 mm sieve size used for the CA and ACQ, and creosote wood analyses was acceptable.

7. Conclusions

Based on the analytical results of copper-based and creosote-treated wood samples, DTSC summarized the following conclusions:

1. Wood products treated by ACQ-C and CA-B contain high level of copper, which exceeds California TTLC and STLC regulatory criteria. Therefore, wood products treated by ACQ-C and CA-B have the potential to be a non-RCRA hazardous waste when disposed.

2. All untreated wood samples were not toxic to fish. The fish survival rate in 500 mg/l bioassay was 100 percent.

3. Creosote-treated railroad ties contain materials toxic to fish. Sampled out-of-service creosote-treated railroad ties have the potential to fail the California regulated acute aquatic 96-hr LC_{50} bioassay. The survival rates in all three Douglas fir out-of-service railroad tie composite samples were less than 50 percent in 500 mg/l bioassay. Therefore, out-of-service creosote-treated railroad ties have the potential to be a non-RCRA hazardous waste when disposed.

4. Treated wood samples can be prepared by cutting lumber into sections, sub-sections, cubes, and further by grinding to obtain a proportional representative treated and non-treated mixture.

5. Visually distinguishing the treated and non-treated areas at the cross sections of both treated copper-base lumber products and out-of-service railroad ties is feasible.

6. It is the generator's responsibility to determine waste classification.

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